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CATALYST FOR PURIFYING EXHAUST GAS

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(56) Prior Art Documents
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(57) Claim

1. A catalyst for purifying exhaust gas comprising a honeycomb carrier of monolithic structure and a coating layer applied on said honeycomb carrier and formed with a catalyst composition comprising a platinum group metal-supporting zirconia produced by depositing said platinum group metal on zirconia powder, a refractory inorganic oxide, and a rare earth metal oxide, said platinum group metal is at least one member selected from the group consisting of (a) rhodium, (b) combination of rhodium and platinum, (c) combination of rhodium and palladium, and (d) combination of rhodium, platinum, and palladium, and is deposited in proportion in the range of 0.5 to 30% by weight on said zirconia powder.



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Complete Specification for the invention entitled:

CATALYST FOR PURIFYING EXHAUST GAS AND METHOD FOR PRODUCTION THEREOF

The following statement is a full description of this invention, including the best method of performing it known to me:

5 This invention relates to a catalyst for purifying exhaust gas. More particularly, it relates to a catalyst for purifying the exhaust gas from the internal combustion engine such as of an automobile for simultaneous removal from the exhaust gas of noxious 10 components such as hydrocarbon (HC), carbon monoxide (CO), and nitrogen oxides (NO_x), which catalyst especially exhibits outstanding durability even when it is used under harsh conditions such as under a high-temperature oxidative atmosphere and manifests a 15 high purifying ability to the aforementioned noxious components at low temperatures.

Description of the Prior Art:

In the conventional noble metal-containing catalyst for purifying the exhaust gas, for the purpose 20 of ensuring effective use of the noble metal contained in a very minute amount in the catalyst, efforts have been made to allow the noble metal to be deposited in as high a degree of dispersion as possible on a refractory inorganic oxide of a large surface area such as 25 activated alumina. The catalyst having the noble metal carried in a high degree of dispersion enjoys a high initial activity. When it is exposed to such harsh conditions as involved under a high-temperature oxidative atmosphere, however, the noble metal gains 30 gradually in particle size, undergoes a chemical conversion into a less active state, and tends to induce a reaction with the carrier substance and cerium oxide. Because the noble metal is deposited in the high degree of dispersion, there tends to ensue a disadvantage that 35 the degradation of catalytic activity is rather heavy.

In this field, zirconia is used more often than not as incorporated chiefly in a carrier substrate for the purpose of stabilizing the physical properties of the catalyst such as specific surface area. To cite 5 a case using zirconia as a carrier substrate for a noble metal, Japanese Patent Publication SHO 57(1982)-29,215 and Japanese Patent Laid-Open SHO57(1982)-153,737 disclose a method which comprises forming on a carrier a coating layer containing alumina and zirconia and 10 subsequently depositing a noble metal thereon. The catalyst produced by the method of this principle, however, suffers from the degradation of catalytic activity due to the same cause as mentioned above because the greater part of the noble metal is 15 substantially dispersed in a high ratio in the alumina.

As carrier substances incapable of interacting with noble metals, particularly rhodium, zirconia (U.S.P. No. 4,233,189) and alpha alumina (U.S.P. No. 4,172,047) have been known in the art. Zirconia and alpha alumina 20 generally possess small surface areas. It has been pointed out, however, that the catalysts having rhodium carried on these substances have a disadvantage that exhibit poor initial activity and possess no satisfactorily high ability to purify the exhaust gas at 25 low temperatures after long term using.

An object of this invention, therefore, is to provide a novel catalyst for purifying the exhaust gas and a method for the production thereof.

Another object of this invention is to provide 30 a catalyst for purifying the exhaust gas which exhibits outstanding durability even when it is used under harsh conditions and possesses a notable ability to purify thoroughly the exhaust gas of the noxious components thereof even at low temperatures and a method for the 35 production thereof.

SUMMARY OF THE INVENTION

The objects of the invention described above are accomplished by a catalyst for purifying the exhaust gas, produced by coating a honeycomb carrier of monolithic structure with a catalyst composition 5 comprising a platinum group metal carrying zirconia obtained by depositing the platinum group metal on zirconia powder, a refractory inorganic oxide, and a rare earth metal oxide.

The objects are also accomplished by a method 10 for the production of a catalyst for purifying the exhaust gas, which method comprises preparing an aqueous slurry containing a platinum group metal-carrying zirconia, a refractory inorganic oxide, and a rare earth metal oxide, coating a honeycomb carrier of monolithic 15 structure with the aqueous slurry, and subsequently calcining the resultant coated carrier.

These objects are further accomplished by a catalyst for purifying the exhaust gas, produced by coating a honeycomb carrier of monolithic structure with 20 a catalyst composition consisting of the following noble metal containing refractory inorganic oxides, the average particle diameter of which is adjusted in the range of 0.5 to 20 microns (A) at least one refractory inorganic oxide selected from the group consisting of 25 (a) a refractory inorganic oxide having carried thereon 5 to 30% by weight of at least one noble metal selected from the group consisting of platinum and palladium and (b) a refractory inorganic oxide having carried thereon 1 to 20% by weight of rhodium or (B) a refractory 30 inorganic oxide having carried thereon 5 to 30% by weight of at least a noble metal selected from the group consisting of platinum and palladium and 1 to 20% by weight of rhodium.

The objects described above are also 35 accomplished by a method for the production of a catalyst for purifying the exhaust gas, which method

comprises preparing a catalyst composition containing refractory inorganic oxides, the average particle diameter of which is adjusted in the range of 0.5 to 20 microns (A) at least one refractory inorganic oxide selected from the group consisting of (a) a refractory inorganic oxide having carried thereon 5 to 30% by weight of at least one noble metal selected from the group consisting of platinum and palladium and (b) a refractory inorganic oxide having carried thereon 1 to 20% by weight of rhodium or (B) a refractory inorganic oxide having carried thereon 5 to 30% by weight of at least one noble metal selected from the group consisting of platinum and palladium and 1 to 20% by weight of rhodium and coating a honeycomb carrier of monolithic structure with the catalyst composition, and subsequently calcining the coated carrier.

The conventional theory is that, the noble metal which must be used in a very minute amount ought to be deposited in a small ratio of deposition on a refractory oxide of a large surface area so that the degree of depression of the noble metal is as high as possible. However, the applicants have found, contrary to this conventional theory, that a noble metal-containing refractory inorganic oxide produced by depositing the noble metal in a high ratio of deposition on a small amount of refractory inorganic oxide gives rise to a catalyst of surprisingly high durability when the aforementioned noble metal-containing refractory inorganic oxide is adjusted in the form of cohesive particles of a relatively large average particle diameter in the range of 0.5 to 20 microns and dispersed in a catalyst coating layer. The present invention has been perfected as the result.

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EXPLANATION OF THE PREFERRED EMBODIMENTS



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The catalyst composition in the first aspect of this invention comprises a zirconia having deposited thereon a platinum group metal at least a rhodium-containing, a refractory inorganic oxide, and a rare earth metal oxide.

The zirconia to be used in the first aspect of this invention possesses a specific surface area exceeding $10 \text{ m}^2/\text{g}$, preferably falling in the range of 60 to $100 \text{ m}^2/\text{g}$. The primary particles of this zirconia 10 possess an average particle diameter of not more than 2,000 Å, preferably not more than 500 Å. A commercially available zirconia may be used on condition that it satisfies these requirements. Otherwise the zirconia may be prepared, for example, by a method which 15 comprises neutralizing an aqueous solution of zirconium salt as with ammonia, washing the product of neutralization, drying and calcining the washed product.

The amount of the zirconia to be used generally is in the range of 0.5 to 50% by weight, based 20 on the amount of the catalyst composition. Even when it is used in an amount falling in the range of 0.5 to 10% by weight, the produced catalyst composition is capable of fully manifesting the effect contemplated by the invention. If the amount of the zirconia exceeds 50% by 25 weight, the individual particles of zirconia gain in growth of particle diameter at an accelerated rate possibly to impair the catalytic activity of the composition. The platinum group metal deposited on the zirconia required to incorporate therein rhodium. 30 Further incorporation of platinum or palladium is observed to bring about an improvement further in the low-temperature activity of the catalyst after long term using at elevated temperatures. The total amount of platinum and palladium to be incorporated in addition to 35 rhodium desirably falls in the range of 1/5 to 5 in gravimetric ratio, based on the amount of rhodium. Thus, the noble metal-carrying zirconia

contains such noble metals in a total concentration falling in the range of 0.5 to 30% by weight, preferably 1 to 20% by weight.

The platinum group metal except for rhodium is not required to be wholly deposited on the zirconia. It may be deposited on a refractory inorganic oxide such as alumina or on a rare earth metal oxide. The deposition of the noble metal on the zirconia may be effected by any of the conventional methods and need not be carried out by any specific method. Rhodium chloride, rhodium nitrate, and rhodium sulfate can be used as rhodium sources and platinic chloride, dinitrodiammne platinum, palladium chloride, and palladium nitrate as platinum or palladium sources, all in the form of an aqueous solution or an alcoholic solution. Where two or more platinum group metals are to be deposited on the zirconia, this deposition may be effected by impregnating the metals either separately or collectively in the solution. Then, by drying and calcining the impregnated zirconia, the noble metals are deposited fast on the zirconia.

As examples of the refractory inorganic oxide to be used effectively in the first aspect of the present invention, there may be cited alumina, silica, titania, magnesia, and zirconia. It is desirable to use alumina, particularly activated alumina among other refractory inorganic oxides cited above. This alumina may be used in any of possible crystalline forms such as γ , δ , θ , α , ζ , κ , and η . Though the refractory inorganic oxide may be directly incorporated in the unmodified form in the catalyst composition, it is ^{possible} ~~enabled to contribute~~ to further enhance the catalyst composition's purifying ability by incorporating therein rare earth metals and such base metal elements as chromium, manganese, iron, cobalt, nickel, and zirconium in the form of oxides in a total amount falling in the



range of 0.1 to 30% by weight, preferably 2 to 20% by weight, based on the amount of the refractory inorganic oxide such as, for example, alumina.

5 As examples of the rare earth metal oxide, there can be cited the oxides of cerium, lanthanum, and neodymium. It is particularly desirable to use cerium oxide among other rare earth metal oxides enumerated above.

10 The rare earth metal oxide can be deposited on the refractory inorganic oxide such as alumina as mentioned above in an amount falling in the range of 0.1 to 30% by weight, preferably 2 to 20% by weight. Otherwise, it can be incorporated directly in the catalyst composition in the form of oxide, carbonate or hydroxide, which may be converted into a corresponding oxide by calcining or through actual use. In the latter case of incorporation, the oxide can be incorporated in the catalyst composition in an amount falling 15 in the range of 5 to 80% by weight, preferably 10 to 50% by weight.

20 In the first aspect of the present invention, if the platinum group metal, particularly the platinum group metal containing rhodium, is stably deposited on the zirconia in the form of microfine particles possessing a very large surface area, the possible adverse effects arising from the interaction between the carrier substance, the rare earth metal oxide, and the base metal oxide is curbed and the catalyst composition is able to incorporate therein the rare 25 earth metal oxide and the base metal oxide in larger amounts than heretofore permitted and, as the result, the catalyst composition is allowed to possess notably improved durability and purifying ability.

30 The zirconia having deposited therein the platinum group metal, particularly the platinum group metal containing rhodium, the rare earth group oxide, and the refractory inorganic oxide which have been



obtained as described above are ground and stirred as in a ball mill to produce an aqueous slurry. A finished catalyst is then produced by coating a honeycomb carrier of monolithic structure with the aqueous slurry, and 5 optionally calcining the dried carrier. This calcining is performed at a temperature in the range of 100° to 600°C, preferably 130° to 300°C for a period in the range of 1 to 10 hours, preferably 1 to 3 hours.

The catalyst composition in the second aspect 10 of the present invention comprises (A) (a) a refractory inorganic oxide having carried therein platinum and/or palladium and/or (b) a refractory inorganic oxide having carried thereon rhodium or (3) a refractory inorganic oxide having carried thereon platinum and/or palladium 15 and rhodium and optionally incorporates therein (C) cerium oxide and/or (D) a refractory inorganic oxide containing no deposited noble metal.

The range of the high ratio of deposition of the noble metal on the refractory inorganic oxide is 5 to 30% by weight, preferably 10 to 20% by weight, in the case of platinum and/or palladium and 1 to 20% by weight, preferably 1 to 10% by weight, in the case of rhodium. If the ratio of deposition of platinum and/or palladium is less than 5% by weight or that of rhodium 25 is less than 1% by weight, the state of dispersion approximates that in the conventional catalyst and the catalyst composition, therefore, incurs heavy degradation of catalytic activity. If the ratio of deposition of platinum and/or palladium exceeds 30% by 30 weight or that of rhodium exceeds 20% by weight, the active sites of the noble metal which contribute effectively to the reaction are not increased but are rather decreased even at the initial stage and as the result the catalyst shows poor initial activity. 35 Moreover, the noble metal entails notable growth of particle size, a phenomenon not observed where the ratio

of deposition falls in the range defined by the present invention. This growth of particle size results in a serious degradation of catalyst activity.

Optionally, platinum and/or palladium and 5 rhodium may be (A) independently deposited on separate portions of the refractory inorganic oxide and the noble metal-carrying refractory inorganic oxide portions consequently obtained may be used either independently or as suitably combined. Otherwise, these noble metals 10 may be (B) collectively deposited on one and the same portion of the refractory inorganic oxide. When the noble metals are collectively deposited on one and the same portion of the refractory inorganic oxide, the total amount of the noble metals so deposited is desired 15 to fall in the range of 6 to 40% by weight, preferably 11 to 30% by weight, in order for the produced catalyst to give satisfactory results. The catalyst durability is improved by having platinum and/or palladium and rhodium deposited both in high ratios. This improvement 20 of durability may be logically explained by a supposition that the interaction between platinum and rhodium, for example, curbs the formation of irreversible rhodium oxide which is not easily reduced to an active rhodium metal. It is also surprising to 25 note that no discernible inactivation of the catalyst is brought about by the alloyage of platinum with rhodium so long as the ratio of deposition falls within the range specified by this invention.

The second characteristic of the second aspect 30 of the present invention resides in the fact that the refractory inorganic oxide having the noble metals deposited thereon in high ratios is dispersed in the form of particles of a relatively large particle diameter falling in the range of 0.5 to 20 microns, 35 preferably 1 to 15 microns. By regulating the average particle diameter in this range, the interaction and the reaction between the noble metals and the refractory

inorgnaic oxide can be mitigated without a sacrifice of the efficiency of the reaction for purifying the exhaust gas.

Owing to the combination of the 5 characteristics described above, the catalyst of this invention which is produced by coating a honeycomb carrier of monolithic structure with 1 to 20g, preferably 2 to 15 g, of the refractory inorganic oxide having noble metals deposited thereon in high ratios and 10 possessing an average particle diameter in the range of 0.5 to 20 microns and 50 to 200 g, preferably 50 to 150 g, of the refractory inorganic oxide containing no noble metal, each per liter of the carrier exhibits highly satisfactory durability under harsh conditions 15 such as under a high-temperature oxidative atmosphere.

For the platinum and palladium to be used in the second aspect, platinic chloride, dinitro-diammine platinum, platinum-sulfite complex, platinum tetramine chloride, palladium chloride, and palladium nitrate, for 20 example, are desirable sources. As rhodium sources, rhodium nitrate, rhodium chloride, rhodium sulfate, rhodium-sulfite complex, and rhodium-ammine complex are desirable.

As examples of the refractory inorganic oxide 25 to be used in this invention, there can be cited alumina, silica, titania, zirconia, alumina-silica, alumina-titania, alumina-zirconia, silica-titania, silica-zirconia, titania-zirconia, and alumina-magnesia.

It is particularly desirable to use alumina, 30 particularly activated alumina, and zirconia among other refractory inorganic oxides enumerated above. The activated alumina is desired to be of a grade possessing a specific surface area in the range of 5 to 200 m^2/g , preferably 50 to 180 m^2/g . This invention does not 35 discriminate the activated alumina on account of the crystalline form thereof. The activated alumina can be used in any of all possible crystalline forms such as

γ , δ , θ , α , ζ , κ , and η . An activated alumina which has at least one element selected from the group consisting of rare earth metals such as lanthanum, cerium, and neodymium, alkaline earth elements such as calcium and barium, and metal elements such as chromium, manganese, iron, cobalt, nickel, and zirconium deposited thereon in the form of an oxide in an amount falling in the range of 0.1 to 30% by weight, preferably 0.2 to 20% by weight, is also usable.

10 In the case of using a zirconia in this invention, it is desirably possessed the zirconia to be used in this invention possesses a specific surface area exceeding at least $10 \text{ m}^2/\text{g}$, preferably falling in the range of 60 to $100 \text{ m}^2/\text{g}$, and an average primary particle 15 diameter not exceeding $2,000 \text{ \AA}$, preferably not exceeding 500 \AA .

A commercially available zirconia may be used so long as it possesses the physical properties specified above. The zirconia of the foregoing 20 description may be prepared, for example, by neutralizing an aqueous solution of zirconia salt as with ammonia and washing with water, drying, and calcining the product of the neutralization. A zirconia which is stabilized with not more than 10% by weight, 25 preferably not more than 8% by weight, of yttrium or an alkaline earth metal such as calcium is also usable.

The catalyst composition made of the aforementioned noble metal-carrying refractory inorganic oxide may incorporate therin cerium oxide when necessary 30 for the purpose of further enhancing the effect thereof.

As the source for the cerium oxide to be used in the second aspect of the present invention, any starting material can be used so long as it is capable of existing as cerium dioxide (CeO_2) in the finished 35 catalyst. For example, commercially available CeO_2 , cerium carbonate, and cerium hydroxide are available as cerium oxide sources. Alternatively, the incorporation

of cerium oxide may be attained by impregnating the refractory inorganic oxide with a cerium salt solution such as, for example, an aqueous cerium nitrate solution. The catalyst of this invention is enabled to 5 manifest the properties thereof to greater advantage by using as a cerium oxide an alumina-modified cerium oxide which is obtained by impregnating a water-insoluble cerium compound with at least one member selected from the group consisting of water-soluble aluminum compounds 10 and alumina hydrates and calcining the product of impregnation.

As examples of the water-insoluble cerium compound, there can be cited cerium oxide, cerium hydroxide, and cerium carbonate. It is particularly 15 desirable to use cerium carbonate among other cerium compounds cited above. This water-insoluble cerium compound is used in the form of fine powder having a particle diameter in the range of 0.1 to 100 microns, preferably 0.2 to 80 microns. As examples of the 20 water-soluble aluminum compound and/or alumina hydrate, there can be cited aluminum nitrate, aluminum chloride, aluminum sulfate, gysprite, bayerite, boehmite, alumina gel, and alumina sol. It is especially desirable to use aluminum nitrate among other water-soluble aluminum 25 compounds cited above.

The amounts of the water-insoluble cerium compound and the water-soluble aluminum compound and/or alumina hydrate to be used are not specifically limited. The use of these compounds permits effective production 30 of an alumina-modified cerium oxide. Desirably, the atomic ratio of cerium to aluminum, Ce/Al, is in the range of 1 to 20, preferably 2 to 10. After the water-insoluble cerium compound is impregnated with the water-soluble aluminum compound and/or the alumina 35 hydrate, the product of this impregnation is generally dried at a temperature in the range of 100° to 300°C and

then calcined in the air at a temperature in the range of 300° to 700°C to give rise to an alumina-modified cerium oxide.

The refractory inorganic oxide having noble metals deposited thereon at high ratios as specified by the present invention is adjusted to an average particle diameter in the range of 0.5 to 20 microns. This adjustment of the average particle diameter is attained, for example, by impregnating the aforementioned refractory inorganic oxide in the form of powder or pellets with noble metal compounds and then pulverizing the product of impregnation as with a mill to a desired particle diameter.

This treatment gives rise to a slurry containing a powder of adjusted particle diameter. By wash coating a honeycomb of monolithic structure with this slurry and then calcining the coated carrier, there is obtained a finished catalyst. The calcination is performed at a temperature falling generally in the range of 100 to 600°C, preferably 130 to 300°C for a period in the range of 1 to 10 hours, preferably 1 to 3 hours.

The honeycomb carrier of monolithic structure to be used in the first and second aspects of the present invention can be any of honeycomb carriers referred to by the generic term "ceramic honeycomb carrier." The honeycomb carriers formed with such materials as cordierite, mullite, α -alumina, zirconia, titania, titanium phosphate, aluminum titanate, petalite, spodumene, alumino silicate, and magnesium silicate prove to be particularly desirable. Those made of cordieritic substance are used particularly advantageously in the catalyst for use in the internal combustion engine among other materials enumerated above. Honeycomb carriers formed in monolithic structure with a metal such as stainless steel or Fe-Cr-Al alloy which is resistant to oxidation and to

heat can be used too. The monolithic carrier of the preceding description can be produced, for example, by the extrusion molding method or the method of tightly rolling a sheetlike element. The openings (cells) 5 formed in the monolithic honeycomb carrier for passage of the gas under treatment may be in a hexagonal, tetragonal, trigonal, or corrugated shape. The honeycomb carrier functions very satisfactorily when the cell density (number of cells per unit cross sectional 10 area) is in the range of 150 to 600 cells/square inch.

Now, the present invention will be described more specifically with reference to working examples. Needless to mention, this invention is not limited only to these working example.

15 Example 1

A 10.0-g portion of zirconia possessing a specific surface area of $70 \text{ m}^2/\text{g}$ and an average particle diameter of 200 \AA (produced by Daiichi Kigenso kagaku K.K.) was impregnated with an aqueous rhodium chloride 20 solution containing 0.3 g of rhodium and the impregnated zirconia was dried at 120°C for 12 hours. Then, the dried zirconia was calcined in the air at 500°C for 1 hour, to produce zirconia powder containing 2.9% by weight of rhodium. Then, 150 g of activated alumina 25 possessing a specific surface area of $150 \text{ m}^2/\text{g}$ was impregnated with an aqueous platinic chloride solution containing 1.5 g of platinum. The impregnated activated alumina was dried at 150°C for 12 hours and then calcined in the air at 500°C for 1 hour, to afford a 30 platinum-containing alumina powder. In a ball mill, the two powders obtained as described above and 75 g of commercially available cerium oxide powder were wet pulverized for 20 hours, to prepare an aqueous slurry. Monolithic carrier pieces of cordierite 33 mm in outside 35 diameter and 76 mm in length containing about 400 gas flow cells per square inch of cross-sectional area were immersed in the aforementioned slurry, removed from the

slurry, then blown with compressed air to remove excess slurry from inside the cells, and dried at 140°C for 3 hours, to produce a catalyst A. This catalyst A, on analysis by the fluorescent X-ray, was found to contain 0.056 g of platinum and 0.011 g of rhodium per catalyst piece.

Example 2

A zirconia powder containing 1.8% by weight of rhodium and 8.9% by weight of platinum was prepared by 10 impregnating 15.0 g of the same zirconia powder as used in Example 1 in a mixture of an aqueous rhodium chloride solution containing 0.3 g of rhodium with an aqueous platinic chloride solution containing 1.5 g of platinum, drying the product of impregnation at 120°C for 12 15 hours, and then calcining the dried powder in the air at 500°C for 1 hour. In a ball mill, the zirconia powder and 145 g of the same activated alumina as used in Example 1 and 75 g of cerium oxide were wet pulverized for 20 hours, to produce an aqueous slurry. A catalyst 20 B was obtained by following the procedure of Example 1 using this aqueous slurry. The catalyst B was found to contain 0.052 g of platinum and 0.010 g of rhodium per catalyst piece.

Example 3

25 A catalyst C was obtained by following the procedure of Example 2, excepting a powder (iron-containing activated alumina) produced by impregnating 140 g of activated alumina with a solution of 25.3 g of ferric nitrate in 100 g of purified water 30 and drying and calcining the product of impregnation was used in the place of the activated alumina of Example 2. The catalyst C was found to contain 0.054 g of platinum and 0.011 g of rhodium per catalyst piece.

Control 1

35 An aqueous slurry was prepared by wet pulverizing 160 g of the same activated alumina and 75 g of the same cerium oxide as used in Example 1 in a ball

mill for 20 hours. Then, by following the procedure of Example 1, monolithic carrier pieces of cordierite were wash coated with the aqueous slurry, dried at 140°C for 3 hours, and then calcined in the air at 500°C for 1 hour. The monolithic carrier pieces so treated were immersed in a mixed aqueous solution of platinic chloride and rhodium chloride, dried and calcined in the air at 400°C for 1 hours, to produce a catalyst I. This catalyst I was found to contain 0.055 g of platinum and 10 0.011 g of rhodium per carrier piece.

Control 2

An aqueous slurry was prepared by wet pulverizing 120 g of the same activated alumina as used in Example 1 and 120 g of a commercially available 15 zirconia powder in a ball mill for 20 hours. Then, by following the procedure of Example 1, monolithic carrier pieces of cordierite were wash coated with the aqueous slurry, dried at 140°C for 3 hours, and calcined in the air at 500°C for 1 hour. The monolithic carrier pieces 20 so treated were immersed in a mixed aqueous solution of platinic chloride and rhodium chloride, dried, and calcined in the air at 400°C for 1 hour, to produce as catalyst II. This catalyst II was found to contain 0.056 g of platinum and 0.011 g of rhodium per carrier 25 piece.

Example 4

A zirconia powder containing 2.3% by weight of rhodium and 20.3% by weight of palladium was prepared by immersing 12.0 g of zirconia possessing a specific 30 surface area of 90 m²/g and an average particle diameter of 150 Å (produced by Daiichi Kigenso Kagaku K.K.) in a mixture of an aqueous rhodium nitrate solution containing 0.35g of rhodium with an aqueous palladium nitrate solution containing 3.15 g of palladium, drying 35 the product of immersion at 120°C for 12 hours, and then calcining the dried immersion product in the air at 500°C for 1 hour.

An alumina powder containing CeO_2 and Fe_2O_3 was obtained by dissolving 56.1g of cerium nitrate and 32.2 g of ferric nitrate in 200 g of purified water, mixing the resultant mixture with 200 g of an activated 5 alumina possessing a specific surface area of $100 \text{ m}^2/\text{g}$, drying the wet mixture at 120°C for 12 hours, and then calcining the dried mixture in the air at 700°C for 1 hour. An aqueous slurry was prepared by wet pulverizing the two powders obtained as described above in a ball 10 mill for 20 hours. By following the procedure of Example 1, monolithic carrier pieces of cordierite were wash coated with the aqueous slurry and dried at 140°C for 3 hours, to produce a catalyst D. This catalyst D was found to contain 0.120 g of palladium and 0.013 g of 15 rhodium per carrier piece.

Example 5

A zirconia powder containing 2.8% by weight of rhodium and 2.8% by weight of palladium was prepared by immersing 12.0 g of the same zirconia as used in Example 20 4 in a mixture of an aqueous rhodium nitrate solution containing 0.35 g of rhodium with an aqueous palladium nitrate solution containing 0.35 g of palladium, drying the product of immersion at 120°C for 12 hours, and then calcining the dried product in the air at 500°C for 1 25 hour.

Then, an aqueous solution of 56.1 g of cerium nitrate and 32.2 g of ferric nitrate in 200 g of purified water and an aqueous palladium nitrate solution containing 2.8 g of palladium were mixed. The resultant 30 mixed solution was mixed with 200 g of an activated alumina possessing a specific surface area of $100 \text{ m}^2/\text{g}$, dried at 120°C for 12 hours, and then calcined in the air at 600°C for 1 hour. In a ball mill, the two 35 powders obtained as described above were wet pulverized for 20 hours, to produce an aqueous slurry. Then, a catalyst E was obtained by following the procedure of

Example 1 using the aqueous slurry. This catalyst E was found to contain 0.121 g of palladium and 0.013 g of rhodium per carrier piece.

Example 6

5 An aqueous slurry was prepared by wet pluverizing a zirconia powder containing 2.3% by weight of rhodium and 20.3% by weight of palladium prepared by following the procedure of Example 4, 150 g of an activated alumina possessing a specific surface area of 10.90 m²/g, and 80 g of cerium oxide in a ball mill for 20 hours. A catalyst F was obtained by following the procedure of Example 1 using the aqueous slurry. This catalyst F was found to contain 0.115 g of palladium and 0.012 g of rhodium per catalyst piece.

15 Control 3

A solution of 56.1 g of cerium nitrate and 32.2 g of ferric nitrate in 200 g of purified water was mixed with 200 g of an activated alumina possessing a specific surface area of 100 m²/g, dried at 120°C for 12 hours, and then calcined in the air at 700°C for 1 hour. An aqueous slurry was prepared by wet pulvverizing the powder obtained as described above in a ball mill for 20 hours. Then, by following the procedure of Example 1, monolithic carrier pieces of cordierite were wash coated 25 with the aqueous slurry, dried at 140°C for 3 hours, and calcined in the air at 500°C for 1 hour. A catalyst III was obtained by immersing the monolithic carrier pieces so treated in a mixed aqueous solution of palladium chloride and rhodium chloride, drying the product of 30 immersion, and then calcining the dry product in the air at 400°C for 1 hour. This catalyst III was found to contain 0.123 g of palladium and 0.013 g of rhodium per carrier piece.

Control 4

35 A powder possessing a specific surface area of 5 m²/g and an average particle diameter of 5,000 Å was obtained by calcining a commercially available zirconia

at 1,000°C for 10 hours. A catalyst IV was obtained by following the procedure of Example 4, excepting the zirconia mentioned above was instead. The catalyst IV was found to contain 0.120 g of palladium and 0.013 g of 5 rhodium per carrier piece.

Example 7

The catalysts of Examples 1 through 3 and the catalysts of Controls 1 and 2 were tested for catalytic property during initial use and after aging in an 10 electric furnace. The aging in the electric furnace was carried out in a high-temperature oxidative atmosphere of air involving very harsh conditions of 900°C and 20 hours.

The evaluation of catalytic property was 15 performed with an electronically controlled engine (4 cylinders 1,800 cc), with the gas temperature at the inlet to a catalyst bed continuously varied from 200°C to 450°C with a heat-exchanger to determine purifying ratios of CO, HC, and NOx. During this evaluation, the 20 engine was operated as vibrated at a rate of 1 Hz, with the space velocity of gas (S.V.) fixed at 90,000 hr⁻¹ and the average air combustion ratio, A/F, at 14.6 ± 0.5. The inlet gas temperatures (T_{50}) at which the purifying ratios of CO, HC, and NOx reached 50% were as 25 shown in Table 1.

The catalyst of Examples 1 through 3 and the catalysts of Controls 1 and 2 were also tested for catalytic property after test run of engine. This test was carried out with an electronically controlled engine 30 (8 cylinder 4,400 cc). With this motor operated in a mode of alternating 60 seconds' steady operation and 6 seconds' decelerated operation (during which period the fuel supply was cut and the catalyst was exposed to a high-temperature oxidative atmosphere) to effect 35 50 hours' aging of the catalyst under conditions such that the catalyst temperature would reach 850°C in the steady operation.

The evaluation of the catalyst property after the test run of engine was carried out by the same procedure as described above. The results are shown in Table 2.

5 Then the catalyst of Examples 4 through 6 and the catalysts of Controls 3 and 4 were tested for catalytic property during initial use and after 50 hours' test run of engine. An electronically controlled engine (6 cylinders 2,400 cc) was used for the test run 10 of engine mentioned above. The endurance test of engine was performed in a mode of alternating 30 seconds' exposure to an oxygen-lean atmosphere and as long exposure to an oxygen-rich atmosphere, introducing secondary air thereby varying the air combustion ratio, 15 A/F, between 14.5 and 17.5. During the test, the catalyst temperature reached the maximum of 950°C.

The evaluation of catalytic property was performed with the same engine as used for the endurance test under the conditions of A/F = 14.6 and SV = 20 approximately $140,000 \text{ hr}^{-1}$, to determine the purifying ratios of HC, CO and NO. In the test during the initial use, the evaluation was made at an inlet temperature of 500°C. In the test after the engine endurance test, the evaluation was made at two inlet temperatures of 500°C 25 and 700°C. The results are shown in Tables 3 and 4.

It is clearly noted from the results that the catalysts of Examples 1 through 3 and the catalysts of Examples 4 through 6 having noble metals deposited on zirconia of large surface area and minute particle 30 diameter possessed highly desirable initial properties

and exhibited very high durability even after harsh endurance conditions as in a high-temperature oxidative atmosphere.

Table 1

5	10	Example 1	Catalyst A	Initial activity			After aging in electric furnace			
				50% conversion temperature (°C)			50% conversion temperature			
				CO	HC	NOx	CO	HC	NOx	
10	2	Example 1	Catalyst A	265	268	264	391	398	390	
				254	259	255	379	383	380	
				254	256	249	371	375	367	
Control 1	2	Control 1	Catalyst A	I	260	264	258	436	443	433
				II	258	262	254	415	423	412

15 Table 2

20	20	Example 1	Catalyst A	After aging by engine						
				50% conversion temperature (°C)			Purifying ratio at 450°C (%)			
				CO	HC	NOx	CO	HC	NOx	
Control 1	2	Control 1	Catalyst A	359	365	355	95	93	93	
				341	347	337	97	95	94	
				340	345	333	97	96	95	
Example 1	2	Example 1	Catalyst A	I	389	397	388	85	88	88
				II	395	402	391	79	83	85

Table 3

		Initial activity			
		Purifying ratio at 500°C (%)			
		CO	HC	NOx	
5	Example 4	Catalyst D	95	95	93
	5	E	96	97	94
	6	F	97	98	97
	Control 3	III	96	97	94
	4	IV	88	90	87

10

Table 4

		After aging by engine						
		Purifying ratio at 500°C (%)			Purifying ratio at 700°C (%)			
		CO	HC	NO	CO	HC	NO	
15	Example 4	Catalyst D	76	85	74	88	93	87
	5	E	82	88	78	91	94	89
	6	F	80	88	77	92	95	88
	Control 3	III	62	71	59	75	82	73
	4	IV	61	73	56	81	86	79

20 Example 8

A catalyst was prepared by using commercially available monolithic carrier pieces of cordierite (produced by NGK Insulators Ltd.). The monolithic carrier pieces were cylinders measuring 33 mm in outside 25 diameter and 76 mm in length, containing about 400 gas flow cells per square inch of cross-sectional area, and possessing a volume of about 65 ml.

An alumina powder containing 16.7% by weight of platinum was prepared by mixing an aqueous solution of the nitrate of dinitro-diammine platinum containing 1.5g of platinum with 7.5g of an activated alumina 5 possessing a specific surface area of 100 m^2/g , thoroughly drying the resultant mixture, and then calcining the dried mixture in the air at 400°C for 2 hours.

An alumina powder containing 9% by weight of 10 rhodium was prepared by mixing an aqueous rhodium nitrate solution containing 0.3 g of rhodium with 3 g of the same activated alumina as described above, thoroughly drying the resultant mixture, and calcining the dried mixture in the air at 400°C for 2 hours.

15 An aqueous slurry for coating was prepared by wet pulverizing 139g of the same activated alumina as described above, the aforementioned platinum-containing alumina powder, and the rhodium-containing alumina powder, in a ball mill for 20 hours. The aforementioned 20 monolithic carrier pieces were immersed in the aqueous slurry for coating, removed from the slurry, and blown with compressed air to remove residual slurry from within the cells and relieve all the cells of clogging slurry. The wet carrier pieces were dried at 130°C for 25 3 hours to obtain a finished catalyst.

The coating layer of this catalyst was photographed at 30 randomly selected spots through an electron probe microanalyzer (EPMA) at 3,000 magnifications to determine the conditions of platinum 30 and rhodium distribution in the layer. It was consequently confirmed that platinum-containing alumina particles and rhodium-containing alumina particles both of an average particle diameter of 5 microns were dispersed in the layer. This catalyst was found to 35 contain 100 g of alumina, 1.0 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

Example 9

A low ratio deposition alumina powder containing 0.2% by weight of rhodium was prepared by mixing an aqueous rhodium nitrate solution containing 0.3 g of rhodium with 142 g of an activated alumina 5 possessing a specific surface area of $120 \text{ m}^2/\text{g}$, drying the resultant mixture, and calcining the dried mixture in the air at 400°C for 2 hours.

A finished catalyst was obtained by following the procedure of Example 8, excepting the aforementioned 10 rhodium-containing alumina powder was used in the place of the alumina powder containing 9% by weight of rhodium and the activated alumina used in Example 8.

When the coating layer of this catalyst was examined by EPMA, the platinum-containing alumina was 15 found to be dispersed in the form of particles of an average particle diameter of 6 microns and no rhodium was detected as dispersed in the form of particles exceeding 0.5 microns in diameter.

This catalyst was found to contain 100 g of 20 alumina, 1.0 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

Example 10

A low ratio deposition alumina powder containing 1% by weight of platinum was prepared by 25 mixing an aqueous solution of the nitrate of dinitro-diammine platinum containing 1.5 g of platinum with 147 g of an activated alumina possessing a specific surface area of $120 \text{ m}^2/\text{g}$, drying the resultant mixture, and then calcining the dried mixture in the air at 400°C 30 for 2 hours.

A finished catalyst was obtained by following the procedure of Example 8, excepting the aforementioned platinum-containing alumina powder was used in the place of the alumina powder containing 16.7% by weight of 35 platinum and the activated alumina as used in Example 8.

When the coating layer of this catalyst was examined by EPMA, the rhodium-containing alumina was dispersed in the form of particles possessing an average

When the coating layer of this catalyst was examined by EPMA, the rhodium-containing alumina was dispersed in the form of particles possessing an average particle diameter of 4.5 microns and no platinum was found to be dispersed in the form of particles exceeding 0.5 microns in diameter. This catalyst was found to contain 100 g of alumina, 1.0 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

Example 11

10 A finished catalyst was obtained by following the procedure of Example 8, excepting an aqueous platinic chloride solution was used in the place of the aqueous solution of the nitrate of dinitro-diammine platinum. The platinum-containing alumina used in this 15 case had 16.8% by weight of platinum deposited thereon.

When the coating layer of this catalyst was examined by EPMA, the platinum-containing alumina was found to be dispersed in the form of particles possessing an average particle diameter of 7 microns and 20 the rhodium-containing alumina in the form of particles possessing an average particle diameter of 4 microns. This catalyst was found to contain 100 g of alumina, 1.0g of platinum, and 0.2 g of rhodium per liter of the catalyst.

25 Example 12

A finished catalyst was obtained by following the procedure of Example 8, excepting an aqueous rhodium chloride solution was used in the place of the aqueous rhodium nitrate solution. The rhodium-containing 30 alumina used in this case had 8.9% by weight of rhodium deposited thereon.

When the coating layer of this catalyst was examined by EPMA, the platinum-containing alumina was found to be dispersed in the form of particles 35 possessing an average particle diameter of 5 microns and the rhodium-containing alumina in the form of particles possessing an average particle diameter of 8 microns.

Example 13

Metallic monolithic carrier cylinders 33 mm in diameter and 76 mm in length were formed by alternately superposing flat thin sheets of aluminum-containing ferrite stainless steel 60 microns in thickness and corrugated sheets produced by corrugating the same flat thin sheets to impart therein waves of a pitch of 2.5 mm. This carrier contained in the cross section thereof about 475 gas flow cells per square inch of 10 cross-sectional area.

A finished catalyst was obtained by following the procedure of Example 8, excepting the aforementioned metallic monolithic carrier was used in the place of the monolithic carrier of cordierite.

15 When the coating layer of this catalyst was examined by EPMA, the platinum-containing alumina was found to be dispersed in the form of particles possessing an average particle diameter of 4 microns and the rhodium-containing alumina in the form of particles 20 possessing an average particle diameter of 3.5 microns. This catalyst was found to contain 100 g of alumina, 1.0g of platinum, and 0.2 g of rhodium per liter of the catalyst.

Example 14

25 An aqueous slurry was obtained by wet pulverizing 139 g of the same activated alumina as used in Example 8 in a ball mill for 13 hours. Further an aqueous slurry for coating was obtained by wet pulverizing the aqueous slurry and the alumina powder 30 containing 16.7% by weight of platinum and the alumina powder containing 9% by weight of rhodium prepared in Example 8 in a ball mill for 7 hours.

When the coating layer of this catalyst was examined by EPMA, the platinum-containing alumina was 35 found to be dispersed in the form of particles possessing an average particle diameter of 15 microns and the rhodium-containing alumina in the form of

particles possessing an average particle diameter of 10 microns. This catalyst was found to contain 100 g of alumina, 1.0 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

5 Control 5

An aqueous slurry was prepared by wet pulverizing 150 g of an activated alumina possessing a specific surface area of 100 m^2/g in a ball mill. The same monolithic carrier of cordierite as used in Example 10 8 was coated with the aqueous slurry.

In a mixed solution obtained by thoroughly stirring an aqueous solution of the nitrate of dinitro-diammine platinum containing 0.065 g of platinum and an aqueous rhodium nitrate solution containing 0.013 15 g of rhodium, the alumina-coated carrier was immersed and allowed to adsorb thereon all the platinum and rhodium present in the solution. The carrier was removed from the solution, treated for removal of the residual solution from within the cells by drainage, 20 dried at 130°C for 3 hours, and then calcined in the air at 400°C for 2 hours, to obtain a finished catalyst.

When the coating layer of this catalyst was examined by EPMA, neither platinum nor rhodium were found to be dispersed in the form of particles exceeding 25 0.5 micron in diameter. This catalyst was found to contain 100 g of alumina, 1.0 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

Control 6

An alumina powder containing 35.7% by weight 30 of platinum was prepared by mixing an aqueous solution of the nitrate of dinitro-diammine platinum containing 1.5 g of platinum with 2.7 g of the same activated alumina as used in Control 5, thoroughly drying the resultant mixture, and then calcining the dried mixture 35 in the air at 400°C for 2 hours.

An alumina powder containing 21.4% by weight of rhodium was prepared by mixing an aqueous rhodium nitrate solution containing 0.3 g of rhodium with 1.1 g of the same activated alumina as described above, 5 thoroughly drying the resultant mixture, and then calcining the dried mixture in the air at 400°C for 2 hours.

A finished catalyst was obtained by following the procedure of Example 8, using the 10 platinum-containing alumina powder and the rhodium-containing alumina powder mentioned above and 146 g of the same activated alumina as used above instead.

When the coating layer of this catalyst was 15 examined by EPMA, the platinum-containing alumina and the rhodium-containing alumina were found to be dispersed in the form of particles possessing an average particle diameter of 6.5 microns. This catalyst was found to contain 100 g of alumina, 1.0 g of platinum, 20 and 0.2 g of rhodium per liter of the catalyst.

Control 7

An aqueous slurry was prepared by wet pulverizing 139 g of activated alumina pellets possessing a specific surface area of $120 \text{ m}^2/\text{g}$ in a ball 25 mill for 19 hours. An aqueous slurry for coating was obtained by wet pulverizing this aqueous slurry and the alumina powder containing 16.7% by weight of platinum and the alumina powder containing 9% by weight of rhodium both prepared as in Example 8 in a ball mill for 30 1 hour. A finished catalyst was obtained by following the procedure of Example 8, using this coating slurry.

When the coating layer of this catalyst was examined by EPMA, the platinum-containing alumina was found to be dispersed in the form of particles 35 possessing an average particle diameter of 30 microns and the rhodium-containing alumina in the form of particles possessing an average particle diameter of 40 microns.

This catalyst was found to contain 100 g of alumina, 1.0 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

Control 8

5 An alumina powder containing 0.2% by weight of rhodium was prepared by mixing an aqueous rhodium nitrate solution containing 0.3 g of rhodium with 150 g of an activated alumina possessing a specific surface area of $120 \text{ m}^2/\text{g}$, drying the resultant mixture, and then 10 calcining the dried mixture in the air at 400°C for 2 hours.

A finished catalyst was obtained by following the procedure of Example 8, excepting the aforementioned rhodium-containing alumina powder and 1.5 g of a 15 commercially available platinum black possessing an average particle diameter of 1.0 micron (produced by Ishifuku Kinzoku Kogyo K.K.) were used instead.

When the coating layer of this catalyst was examined by EPMA, the platinum was found to be dispersed 20 in the form of particles possessing an average particle diameter of 1 micron. This catalyst was found to contain 100 g of alumina, 1.0 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

Example 15

25 The catalysts of Examples 8 through 14 and the catalysts of Controls 5 through 8 were tested for catalytic property after aging in the electric furnace.

This aging in the electric furnace was performed by exposing a given catalyst to a 30 high-temperature oxidative atmosphere involving very harsh conditions of 10 hours' heating at 900°C .

The evaluation of the catalytic property was carried out by using a commercially available electronically controlled engine (4 cylinders 1,800 cc), 35 with a multi-converter packed with the catalyst under treatment and connected to the exhaust system of the engine. The engine was operated, with the air

combustion ratio, A/F, fixed at 14.6. By means of a heat-exchanger which was inserted in front of the catalyst converter in the exhaust system of the engine, the inlet gas temperature was continuously varied from 5 300°C to 500°C. The gas was sampled at the inlet and the outlet of the catalyst converter and analyzed to determine the purifying ratios of CO, HC, and NO and evaluate the purifying ability of the catalyst at low temperatures.

10 The purifying ratios of CO, HC, and NO obtained as described above as the functions of the inlet gas temperature were plotted on a graph to find the inlet gas temperatures (T_{50}) showing a fixed purifying ratio of 50%. The inlet gas temperatures 15 (T_{50}) thus determined were used as the standard for evaluation of the purifying property of catalyst at low temperatures.

20 The results obtained by the method of evaluation of catalytic property described above are shown in Table 5.

Table 5 Evaluation of catalytic property after aging in electric furnace

Catalyst	Purifying property at low temperatures		
	CO purifying temperature, T ₅₀ (°C)	HC purifying temperature, T ₅₀ (°C)	NO purifying temperature, T ₅₀ (°C)
Example 8	395	399	393
9	410	414	408
10	402	408	400
11	400	404	397
12	398	404	396
13	393	398	390
14	398	405	397
Control 5	465	468	465
15	450	455	449
6	446	450	445
7	462	465	462

Then, the catalysts of Examples 8 through 14 and the catalysts of Controls 5 through 8 were tested 20 for catalytic activity after the endurance test in an engine.

This endurance test was performed by using a commercially available electronically controlled engine (8 cylinders 4,400 cc), with a multi-converter packed 25 with a catalyst under test and connected to the exhaust system of the engine. The engine was operated in a mode of alternating 60 seconds' steady operation and 6 seconds' decelerated operation (during which period the supply of fuel was cut and the catalyst was exposed to 30 harsh conditions of a high-temperature oxidative atmosphere), with the catalyst exposed to 50 hours' aging under conditions such that the inlet gas temperature would reach 800°C during the steady operation.

The evaluation of the catalytic property after the endurance test in the engine was carried out in entirely the same manner as in the evaluation of the catalytic property after the aging in the electric furnace described above. The data consequently obtained were compared with those of the purifying property at low temperatures. The results are shown in Table 6 below.

10 Table 6 Evaluation of catalytic property
after test run of engine

Catalyst	Purifying property at low temperatures		
	CO purifying temperature, T ₅₀ (°C)	HC purifying temperature, T ₅₀ (°C)	NO purifying temperature, T ₅₀ (°C)
15	Example 8	375	380
	9	388	380
	10	385	392
	11	379	385
	12	377	385
20	13	373	380
	14	378	386
	Control 5	440	447
25	6	430	436
	7	425	430
	8	440	446

It is clearly noted from Tables 5 and 6 that the catalysts of Examples 8 through 14 in which refractory inorganic oxides having platinum and/or rhodium deposited in high ratios as contemplated by the 30 present invention were dispersed in the form of particles possessing an average particle diameter in the

range of 0.5 to 20 microns invariably exhibited better catalytic properties than the catalysts of Control 5 which had noble metals dispersed in the conventional state. The catalyst of Control 6 which had platinum 5 deposited in a ratio of not less than 30% by weight and rhodium in a ratio of not less than 20% by weight, the catalyst of Control 7 which had platinum and rhodium deposited in ratios falling in the range specified by the present invention and but had these noble metals 10 dispersed in the form of particles exceeding 30 microns in diameter, and the catalyst of Control 8 which had no platinum deposited on a refractory inorganic oxide invariably exhibited poor catalytic properties.

From the foregoing results, it is clear that 15 the catalysts having platinum and rhodium deposited and dispersed under the conditions contemplated by the present invention incur only slight deterioration and exhibit highly satisfactory durability not only under the ordinary conditions of engine operation but also 20 under harsh conditions as in a high-temperature oxidative atmosphere.

Example 16

A finished catalyst was obtained by following the procedure of Example 8, excepting 75 g of a 25 commercially available cerium oxide powder (produced by Nissan Kigenso K.K.) was incorporated in addition to 139 g of the activated alumina, the platinum-containing alumina powder, and the rhodium-containing alumina powder.

30 When the coating layer of this catalyst was examined by the same method as used in Example 8, the platinum-containing alumina and the rhodium-containing alumina were found to be dispersed in the form of particles possessing an average particle diameter of 5 35 microns. This catalyst was found to contain 100 g of alumina, 1.0 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

Example 17

An alumina powder containing 0.2% by weight rhodium was prepared by mixing an aqueous rhodium nitrate solution containing 0.3 g of rhodium with 142 g of an activated aluminum possessing a specific surface area of $120 \text{ m}^2/\text{g}$, drying the resultant mixture, and then calcining the dried mixture in the air at 400°C for 2 hours.

A finished catalyst was obtained by following 10 the procedure of Example 16, excepting the rhodium-containing alumina powder was used in the place of the alumina powder containing 9% by weight of rhodium plus the activated alumina used in Example 16.

When the coating layer of this catalyst was 15 examined by the same method as in Example 8, the platinum-containing alumina was found to be dispersed in the form of particles possessing an average particle diameter of 6 microns and no rhodium was found to be dispersed in the form of particles exceeding 0.5 microns 20 in diameter. This catalyst was found to contain 100 g of alumina, 50 g of cerium oxide, 1.0 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

Example 18

An alumina powder containing 1% by weight of 25 platinum was prepared by mixing an aqueous solution of the nitrate of dinitro-diammine platinum containing 1.5 g of platinum with 147 g of an activated alumina possessing a specific surface area of $120 \text{ m}^2/\text{g}$, drying the resultant mixture, and then calcining the dried 30 mixture in the air at 400°C for 2 hours.

A finished catalyst was obtained by following the procedure of Example 16, excepting the platinum-containing alumina powder was used in the place of the alumina powder containing 16.7% by weight of 35 platinum and the activated alumina used in Example 16.

When the coating layer of this catalysts was examined by the same method as in Example 8, the rhodium-containing alumina was found to be dispersed in the form of particles possessing an average particle 5 diameter of 4.5 microns and no platinum was found to be dispersed in the form of particles exceeding 0.5 micron in diameter. This catalyst was found to contain 100 g of alumina, 50 g of cerium oxide, 1.0 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

10 Example 19

A finished catalyst was obtained by following the procedure of Example 16, excepting an aqueous platinic chloride solution was used in the place of the aqueous solution of the nitrate of dinitro-diammine 15 platinum. The platinum-containing alumina used in this case had 16.6% by weight of platinum deposited thereon.

When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum-containing alumina was found to be dispersed in 20 the form of particles possessing an average particle diameter of 7 microns and the rhodium-containing alumina in the form of particles possessing an average particle diameter of 4 microns. This catalyst was found to contain 100 g of alumina, 50 g of cerium oxide, 1.0 g of 25 platinum, and 0.2 g of rhodium per liter of the catalyst.

Example 20

A finished catalyst was obtained by following the procedure of Example 16, excepting an aqueous 30 rhodium chloride was used in the place of the aqueous rhodium nitrate. The rhodium-containing alumina used in this case had 9.1% by weight of rhodium deposited thereon.

When the coating layer of this catalyst was 35 examined by the same method as in Example 8, the platinum-containing alumina was found to be dispersed in the form of particles possessing an average particle

diameter of 5 microns and the rhodium-containing alumina in the form of particles possessing an average particle diameter of 8 microns. This catalyst was found to contain 100 g of alumina, 50 g of cerium oxide, 0.1 g of 5 platinum, and 0.2 g of rhodium per liter of the catalyst.

Example 21

An alumina-modified cerium oxide (atomic ratio of Ce/Al = 5) was prepared by thoroughly mixing 150 ml 10 of an aqueous solution having dissolved therein 65.3 g of aluminum nitrate $[Al(NO_3)_3 \cdot 9H_2O]$ with 319 g of cerium carbonate powder (possessing a Ce content of 47% by weight as CeO_2), drying the resultant mixture at 130°C for 5 hours, and then calcining the dried mixture 15 in the air at 500°C for 1 hour.

A finished catalyst was obtained by following the procedure of Example 16, excepting 75 g of the alumina-modified cerium oxide was used in the place of the commercially available cerium oxide powder.

20 When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum-containing aluminum and the rhodium-containing alumina were both found to be dispersed in the form of particles possessing an average particle diameter of 6 25 microns. This catalyst was found to contain 100 g of alumina, alumina-modified cerium oxide (atomic ratio of Ce/Al = 5), 1.0 g of platinum, and 0.2 g of rhodium.

Example 22

An alumina-modified cerium oxide (atomic ratio 30 of Ce/Al = 8) was prepared by thoroughly mixing 220 ml of an aqueous solution having dissolved therein 54.4 g of aluminum nitrate $[Al(NO_3)_3 \cdot 9H_2O]$ with 426 g of cerium carbonate powder (possessing a Ce content of 47% by weight as CeO_2), drying the resultant mixture at 35 130°C for 5 hours, and then calcining the dried mixture in the air at 500°C for 1 hour.

A finished catalyst was obtained by following the procedure of Example 16, excepting 75g of the alumina-modified cerium oxide was used in the place of the commercially available cerium oxide powder.

5 When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum-containing alumina and the rhodium-containing alumina were both found to be dispersed in the form of particles possessing an average particle diameter of 6 10 microns. This catalyst was found to contain 100 g of alumina, 50 g of alumina-modified cerium oxide (atomic ratio of Ce/Al = 8), 1.0 g of platinum, and 0.2g of rhodium per liter of the catalyst.

Example 23

15 An alumina-modified cerium oxide (atomic ratio of Ce/Al = 5) was prepared by mixing 94.7 g of alumina sol (containing 10% by weight as alumina), 340 g of cerium carbonate (possessing a Ce content of 47% by weight as CeO_2), and 100 ml of water, drying the 20 resultant mixture at 130°C for 5 hours, and then calcining the dried mixture in the air at 500°C for 1 hour.

25 A finished catalyst was obtained by following the procedure of Example 16, excepting 75 of the alumina-modified cerium oxide was used in the place of the commercially available cerium oxide powder.

30 When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum-containing alumina and the rhodium-containing alumina were both found to be dispersed in the form of particles possessing an average particle diameter of 6 35 microns. This catalyst was found to contain 100 g of alumina, 50 g of alumina-modified cerium oxide (atomic ratio of Ce/Al = 5), 1.0 g of platinum, and 0.2 of rhodium per liter of the catalyst.

Example 24

A finished catalyst was obtained by following the procedure of Example 16, excepting the same metallic monolithic carrier as in Example 13 was used in the place of the monolithic carrier of cordierite.

5 When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum-containing alumina was found to be dispersed in the form of particles possessing an average particle diameter of 4 microns and the rhodium-containing alumina 10 in the form of particles possessing an average particle diameter of 3.5 microns. This catalyst was found to contain 100 g of alumina, 50 g of cerium oxide, 1.0 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

15 Example 25

An aqueous slurry was prepared by wet pulverizing 139 g of the same activated alumina as used in Example 16 with 75 g of commercially available cerium oxide in a ball mill for 13 hours. Further an aqueous 20 slurry for coating was prepared by wet pulverizing the aqueous slurry and the alumina powder containing 16.7% by weight of platinum and the powder containing 9% by weight of rhodium prepared as in Example 16 in a ball mill for 7 hours. A finished catalyst was obtained by 25 following the procedure of Example 16, using the aqueous slurry for coating.

When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum-containing alumina was found to be dispersed in 30 the form of particle possessing an average particle diameter of 15 microns and the rhodium-containing alumina in the form of particles possessing an average particle diameter of 10 microns. This catalyst was found to contain 100 g of alumina, 50 g of cerium oxide, 35 1.0 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

Control 9

A catalyst was obtained by following the procedure of Example 5, excepting 75 g of a commercially available cerium oxide powder was incorporated in addition to 150 g of the same activated alumina as used 5 in Example 16.

When the coating layer of this catalyst was examined by the same method as in Example 8, neither platinum nor rhodium was found to be dispersed in the form of particles exceeding 0.5 micron in diameter. 10 This catalyst was found to contain 100 g of alumina, 50 g of cerium oxide, 1.0 g of platinum, and 0.2 of rhodium per liter of the catalyst.

Control 10

A finished catalyst was obtained by following 15 the procedure of Control 6, excepting 75 g of cerium oxide was further incorporated during the course of mixture of the powder.

When the coating layer of this catalyst was examined by the same method as in Example 8, the 20 platinum-containing alumina and the rhodium-containing alumina were both found to be dispersed in the form of particles possessing an average particle diameter of 8 microns. This catalyst was found to contain 100 g of alumina, 50 g of cerium oxide, 1.0 g of platinum, and 25 0.2 g of rhodium per liter of the catalyst.

Control 11

A finished catalyst was obtained by following the procedure of Control 7, excepting 75 g of cerium oxide was further incorporated during the course of 30 mixture of the powders.

When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum-containing alumina was found to be dispersed in the form of particles possessing an average particle 35 diameter of 30 microns and the rhodium-containing alumina in the form of particles possessing an average particle diameter of 40 microns. This catalyst was found

to contain 100 g of alumina, 50 g of cerium oxide, 1.0 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

Control 12

5 A finished catalyst was obtained by following the procedure of Control 8, excepting 75 g of cerium oxide was further incorporated during the mixture of the powders.

When the coating layer of this catalyst was 10 examined by the same method as in Example 8, platinum was found to be dispersed in the form of particles possessing an average particle diameter of 1 micron and no rhodium was found to be dispersed in the form of particles exceeding 0.5 micron in diameter. This 15 catalyst was found to contain 100 g of alumina, 50 g of cerium oxide, 1.0 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

Example 26

20 The catalysts of Examples 16 through 25 and the catalysts of Controls 9 through 12 were tested for catalytic property at low temperature after the aging in an electric furnace and after the endurance test in an engine by following the procedure of Example 15. The 25 three way performance of each catalyst evaluated by the same engine as Example 8. The evaluation conditions were as follows:

The catalyst inlet gas temperature was maintained at 450°C, and the space velocity was adjusted to 90,000 hr⁻¹. The air-fuel ratio was changed 30 continuously from 15.1 to 14.1 with the perturbation condition of ± 0.5 A/F 1.0 Hz by external control, and at the same time the catalyst inlet gas and the catalyst outlet gas were simultaneously analyzed. The CO, HC, and NO purifying ratios of each catalyst were 35 calculated from the inlet and outlet gas analysis data, and plotted against the air-fuel ratio on graphs. The crossover point was defined as the purifying ratio value

at the crossing point between the CO purifying curve and the NO purifying curve. The crossover point and the HC purifying ratio at the air-fuel ratio of the crossover point were used as the standard for evaluation of the three way performance. The results are respectively shown in Table 7 and Table 8.

Table 7 Evaluation of catalytic property
after aging in electric furnace

Catalyst	Three way performance		Purifying property at low temperatures		
	Crossover point	CO, NO purifying ratio (%)	CO purifying temperature	HC purifying temperature	NO purifying temperature
			T ₅₀ (°C)	T ₅₀ (°C)	T ₅₀ (°C)
Example 6	88	87	386	390	385
	17	80	403	407	400
	18	83	395	400	392
19	87	86	388	393	386
20	89	88	385	388	383
21	94	96	370	375	366
22	93	94	373	377	370
23	91	94	375	379	373
24	89	89	382	385	380
25	86	86	390	395	388
Control 9	51	60	443	447	441
10	63	68	427	430	426
11	65	72	420	425	418
30	12	49	445	449	444

Table 8 Evaluation of catalytic property
after test run of engine

Catalyst	Three way performacne		Purifying property at low temperatures		
	Crossover point	CO purifying temperature	HC purifying temperature	NO purifying temperature	
Example 16	87	93	356	360	350
17	80	90	365	370	360
18	83	92	361	365	355
19	86	93	358	363	351
20	87	93	357	363	352
21	94	98	340	345	334
22	92	97	342	346	335
23	93	97	344	349	339
24	89	94	353	358	347
25	85	91	360	364	354
Control 9	73	83	393	401	390
10	75	85	393	400	389
11	77	86	382	390	376
12	70	81	395	403	390

25 It is clearly noted from Tables 7 and 8 that the catalysts of Examples 16 through 25 in which refractory inorganic oxides having platinum and/or rhodium deposited in high ratios as contemplated by the present invention were dispersed in the form of 30 particles possessing an average particle diameter in the range of 0.5 to 20 microns invariably exhibited better catalytic property than the catalyst of Control 9 having the noble metals deposited and dispersed in the conventional states. The catalyst of Control 10 which 35 had platinum deposited in a ratio of not less than 30% by weight and rhodium in a ratio of not less than 20% by

weight, the catalyst of Control 11 which had platinum and rhodium deposited at ratios both falling within the ranges contemplated by this invention but dispersed in the form of particles exceeding 30 microns in diameter, 5 and the catalyst of Control 12 which had no platinum deposited on a refractory inorganic oxide invariably exhibited poor properties.

The catalysts of Examples 21 through 23 which used alumina-modified cerium oxide as a cerium oxide 10 exhibited still better properties.

Example 27

An alumina powder containing 16.1% by weight of platinum and 3.2% by weight of rhodium was prepared by mixing 7.5 g of an activated alumina possessing a 15 specific surface area of $100 \text{ m}^2/\text{g}$ with a mixture of an aqueous solution of the nitrate of dinitro-ammime platinum containing 1.5 g of platinum and an aqueous rhodium nitrate solution containing 0.3 g of rhodium, thoroughly drying the resultant mixture, and then 20 calcining the dried mixture in the air at 400°C for 2 hours.

An aqueous slurry for coating was prepared by wet pulverizing 139 g of the same activated alumina as described above and the platinum and rhodium-containing 25 alumina powder in a ball mill for 20 hours. The same monolithic carrier as used in Example 8 was immersed in this aqueous slurry for coating, removed from the slurry, and then blown with compressed air to remove excess slurry from within the cells and relieve all the 30 cells of clogging slurry. Then, the wet carrier was calcined at 130°C for 3 hours, to obtain a finished catalyst.

When the coating layer of this catalyst was examined by the same method as in Example 8, the 35 platinum- and rhodium-containing alumina was found to be dispersed in the form of particles possessing an average

particle diameter of 4 microns. This catalyst was found to contain 100 g of alumina, 1.0 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

Control 13

5 An alumina powder containing 0.99% by weight of platinum and 0.2% by weight of rhodium was prepared by mixing 150 g of the same activated alumina as used in Example 27 with a mixture of an aqueous solution of the nitrate of dinitro-diammine platinum containing 1.5 g of 10 platinum and an aqueous rhodium nitrate solution, thoroughly drying the resultant mixture, and then calcining the dried mixture in the air at 400°C for 2 hours. A finished catalyst was obtained by following the procedure of Example 27, using the aforementioned 15 alumina powder containing platinum and rhodium.

When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum- and rhodium-containing alumina was not found to be dispersed in the form of particles exceeding 0.5 20 micron in diameter. This catalyst was found to contain 100 g of alumina, 1.0 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

Example 28

A finished catalyst was obtained by following 25 the procedure of Example 27, excepting an aqueous platinic chloride solution was used in the place of the aqueous solution of the nitrate of dinitro-diammine platinum. The platinum- and rhodium-containing alumina had 16.4% by weight of platinum and 3.1% by weight of 30 rhodium deposited thereon.

When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum- and rhodium-containing alumina was found to be dispersed in the form of particles possessing an average 35 particle diameter of 7 microns. This catalyst was found to contain 100 g of alumina, 1.0 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

Example 29

A finished catalyst was obtained by following the procedure of Example 27, excepting an aqueous rhodium chloride solution was used in the place of the 5 aqueous rhodium nitrate solution. The platinum- and rhodium-containing alumina used in this had 16.1% by weight of platinum and 3.3% by weight of rhodium deposited thereon.

When the coating layer of this catalyst was 10 examined by the same method as in Example 8, the platinum- and rhodium-containing alumina was found to be dispersed in the form of particles possessing an average particle diameter of 5 microns. This catalyst was found to contain 100 g of alumina, 1.0 g of platinum, and 0.2 15 g of rhodium per liter of the catalyst.

Example 30

An alumina powder containing 11.4% by weight of platinum and 3.4% by weight of rhodium was prepared by mixing 7.5 g of an activated alumina possessing a 20 specific surface area of $120 \text{ m}^2/\text{g}$ with a mixture of an aqueous solution the nitrate of dinitro-diammine platinum containing 1.0 g of platinum and an aqueous rhodium nitrate solution containing 0.3g of rhodium, thoroughly drying the resultant mixture, and then 25 calcining the dried mixture in the air at 400°C for 2 hours.

A finished catalyst was obtained by following the procedure of Example 27, excepting the platinum- and rhodium-containing alumina was used in the place of the 30 alumina powder containing 16.1% by weight of platinum and 3.2% by weight of rhodium.

When the coating layer of this catalyst was examined by EPMA, the platinum- and rhodium-containing alumina was found to be dispersed in the form of 35 particles possessing an average particle diameter of 5

microns. This catalyst was found to contain 100 g of alumina, 0.67 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

Example 31

5 A finished catalyst was obtained by following the procedure of Example 27, excepting the same metallic monolithic carrier as used in Example 13 was used in the place of the monolithic carrier of cordierite. The platinum- and rhodium-containing alumina used in this 10 case contained 16.3% by weight of platinum and 3.2% by weight of rhodium.

When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum- and rhodium-containing alumina was found to be 15 dispersed in the form of particles possessing an average particle diameter of 4 microns. This catalyst was found to contain 100 g of alumina, 1.0 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

Example 32

20 An aqueous slurry was prepared by wet pulverizing 139 g of the same activated alumina as used in Example 27 in a ball mill for 13 hours. An aqueous slurry for coating was prepared by wet pulverizing the aqueous slurry and the same alumina powder containing 25 16.1% by weight of platinum and 3.2% by weight of rhodium as in Example 27 in a ball mill for 7 hours. A finished catalyst was obtained by following the procedure of Example 27, using the aqueous slurry for coating.

30 When the coating layer of the catalyst was examined by the same method as in Example 8, the platinum- and rhodium-containing alumina was found to be dispersed in the form of particles possessing an average particle diameter of 15 microns. This catalyst was 35 found to contain 100 g of alumina, 1.0 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

Example 33

The catalysts of Examples 27 through 32 and the catalyst of Control 13 were tested for catalytic property after aging in an electric furnace and for catalytic activity after endurance test in an engine in 5 the same manner as in Example 15. The results are shown respectively in Table 9 and Table 10.

Table 9 Evaluation of catalytic property
after aging in electric furnace

5	Catalyst	Purifying property at low temperatures		
		Co purifying temperature, T_{50} (°C)	HC purifying temperature, T_{50} (°C)	NO purifying temperature, T_{50} (°C)
10	Example 27	385	390	382
	28	390	394	388
	29	388	392	385
	30	395	399	392
	31	386	390	382
	32	393	397	390
	Control 13	465	468	465

Table 10 Evaluation of catalytic property
after test run of engine

15	Catalyst	Purifying property at low temperatures		
		Co purifying temperature, T_{50} (°C)	HC purifying temperature, T_{50} (°C)	NO purifying temperature, T_{50} (°C)
20	Example 27	364	370	359
	28	369	375	364
	29	367	374	361
	30	375	382	370
	31	363	369	357
	32	373	380	368
	Control 13	440	447	436

It is clearly noted from Table 9 and Table 10 that the catalysts of Examples 27 through 32 in which refractory inorganic oxides having platinum and rhodium deposited in high ratios contemplated by this invention 5 were dispersed in the form of particles possessing an average particle diameter in the range of 0.5 to 20 microns exhibited far better catalytic properties than the catalyst of Control 13 having noble metals deposited in the conventional state.

10 Example 34

A finished catalyst was obtained by following the procedure of Example 27, excepting 75 g of a commercially available cerium oxide powder (produced by Nissan Kigenso K.K.) was additionally used with 139 g of 15 the activated alumina and the platinum- and rhodium-containing alumina powder.

When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum- and rhodium-containing alumina was found to be 20 dispersed in the form of particles possessing an average particle diameter of 4 microns. This catalyst was found to contain 100 g of alumina, 50 g of cerium oxide, 1.0 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

25 Control 14

A finished catalyst was obtained by following the procedure of Example 34, excepting 75 g of the same commercially available cerium oxide powder as used in Example 34 was used in addition to the platinum- and 30 rhodium-containing alumina powder obtained as in Control 13.

When the coating layer of this catalyst was examined by the same method as in Example 8, neither platinum nor rhodium was found to be dispersed in the 35 form of particles exceeding 0.5 micron in diameter.

This catalyst was found to contain 100 g of alumina, 50 g of cerium oxide, 1.0 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

Example 35

5 A finished catalyst was obtained by following the procedure of Example 34, excepting an aqueous platinic chloride solution was used in the place of the aqueous solution of the nitrate of dinitro-diammine platinum. The platinum- and rhodium-containing alumina 10 used in this case contained 16.0% by weight of platinum and 3.3% by weight of rhodium.

When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum- and rhodium-containing alumina was found be 15 dispersed in the form of particles possessing an average particle diameter of 7 microns. This catalyst was found to contain 100 g of alumina, 50 g of cerium oxide, 1.0 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

20 Example 36

A finished catalyst was obtained by following the procedure of Example 34, excepting an aqueous rhodium chloride solution was used in the place of the aqueous rhodium nitrate solution. The platinum- and 25 rhodium-containing alumina used in this case contained 16.1% by weight of platinum and 3.1% by weight of rhodium.

When the coating layer of this catalyst was examined by the same method as in Example 8, the 30 platinum- and rhodium-containing alumina was found to be dispersed in the form of particles possessing an average particle diameter of 5 microns. This catalyst was found to contain 100 g of alumina, 50 g of cerium oxide, 1.0 g of platinum, and 0.2 g of rhodium per liter of the 35 catalyst.

Example 37

A finished catalyst was obtained by following the procedure of Example 34, excepting the same platinum- and rhodium-containing alumina as obtained in Example 30 was used in the place of the 5 rhodium-containing alumina powder containing 16.1% by weight of platinum and 3.2% by weight of rhodium.

When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum- and rhodium-containing alumina was found to be 10 dispersed in the form of particles possessing an average particle diameter of 5 microns. This catalyst was found to contain 100 g of alumina, 50 g of cerium oxide, 0.67 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

15 Example 38

A finished catalyst was obtained by following the procedure of Example 34, excepting the same metallic monolithic carrier as in Example 13 was used in the place of the monolithic carrier of cordierite.

20 When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum- and rhodium-containing alumina was found to be dispersed in the form of particles possessing an average particle diameter of 4 microns. This catalyst was found 25 to contain 100 g of alumina, 50 g of cerium oxide, 1.0 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

Example 39

30 A finished catalyst was obtained by following the procedure of Example 34, excepting 75 g of the same alumina-modified cerium oxide as in Example 21 was used in the place of the commercially available cerium oxide powder.

When the coating layer of this catalyst was 35 examined by the same method as in Example 8, the platinum- and rhodium-containing alumina was found to be dispersed in the form of particles possessing an average

particle diameter of 6 microns. This catalyst was found to contain 100 g of alumina, 50 g of alumina-modified cerium oxide (atomic ratio of Ce/Al = 5), 1.0 g of platinum, and 0.2 g of rhodium per liter of the 5 catalyst.

Example 40

A finished catalyst was obtained by following the procedure of Example 34, excepting 75 g of the same alumina-modified cerium oxide as in Example 22 was used 10 in the place of the commercially available cerium oxide powder.

When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum- and rhodium-containing alumina was found to be 15 dispersed in the form of particles possessing an average particle diameter of 6 microns. This catalyst was found to contain 100 g of alumina, 50 g of alumina-modified cerium oxide (atomic ratio of Ce/Al = 8), 1.0 g of platinum, and 0.2 g of rhodium per liter of the 20 catalyst.

Example 41

A finished catalyst was obtained by following the procedure of Example 34, excepting 75 g of the same alumina-modified cerium oxide as in Example 23 was used 25 in the place of the commercially available cerium oxide powder.

When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum- and rhodium-containing alumina was found to be 30 dispersed in the form of particles possessing an average particle diameter of 6 microns. This catalyst was found to contain 100 g of alumina, 50 g of alumina-modified cerium oxide (atomic ratio of Ce/Al = 5), 1.0 g of platinum, and 0.2 g of rhodium per liter of the 35 catalyst.

Example 42

An aqueous slurry was prepared by wet pulverizing 139 g of the same activated alumina as used in Example 34 and 75 g of a commercially available cerium oxide in a ball mill for 13 hours. An aqueous 5 slurry for coating was prepared by wet pulverizing the aqueous slurry and the alumina powder containing 16.1% by weight of platinum and 3.2% by weight of rhodium as prepared in Example 34 in a ball mill for 7 hours. A finished catalyst was obtained by following the 10 procedure of Example 34, using the aforementioned aqueous slurry for coating.

When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum- and rhodium-containing alumina was found to be 15 dispersed in the form of particles possessing an average particle diameter of 15 microns. This catalyst was found to contain 100 g of alumina, 50 g of cerium oxide, 1.0 g of platinum, and 0.2 g of rhodium per liter of the catalyst.

20 Example 43

The catalysts of Examples 34 through 42 and the catalyst of Control 14 were tested for catalytic property after aging in an electric furnace and for catalytic activity after endurance test in an engine in 25 the same manner as in Example 15. The results are shown in Table 11 and Table 12.

Table 11 Evaluation of catalytic property
after aging in electric furnace

Catalyst	Three way performance		Purifying property at low temperatures		
	Crossover point		CO purifying temperature	HC purifying temperature	NO purifying temperature
	CO,NO purify-ing ratio(%)	HC purify-ing ratio(%)	T_{50} (°C)	T_{50} (°C)	T_{50} (°C)
Example 34	90	91	380	385	377
35	88	88	384	390	381
36	89	90	382	388	378
37	85	86	390	396	388
38	91	92	379	385	376
39	94	96	370	375	367
40	92	93	373	378	370
41	92	93	372	376	368
42	87	88	390	395	387
Control 14	51	60	443	447	441

Table 12 Evaluation of catalytic property
after test run of engine

Catalyst	Three way performance		Purifying property at low temperatures		
	Crossover point		CO purifying temperature	HC purifying temperature	NO purifying temperature
	CO, NO purify- ing ratio(%)	HC purify- ing ratio(%)	T_{50} (°C)	T_{50} (°C)	T_{50} (°C)
Example 34	90	95	348	353	341
	35	87	354	360	348
	36	88	352	358	345
	37	85	360	366	354
	38	91	347	353	340
	39	95	340	345	334
	40	93	342	348	336
	41	93	342	347	335
	42	86	358	362	351
	Control 14	73	393	401	390

It is clearly noted from Table 11 and Table 12 that the catalysts of Examples 34 through 42 in which refractory inorganic oxides having platinum and rhodium deposited in high ratios as contemplated by the present invention were dispersed in the form of particles possessing an average particle diameter in the range of 0.5 to 20 microns invariably exhibited better properties than the catalyst of Control 14 having noble metals deposited in the conventional state. Particularly the catalysts of Example 36 through 41 which used alumina-modified oxides as cerium oxide exhibited notable satisfactory properties.

Example 44

A zirconia powder containing 16.7% by weight of platinum was prepared by mixing an aqueous solution of the nitrate of dinitro-diammine platinum containing 1.5 g of platinum with 7.5 g of zirconia possessing a specific surface area of $60 \text{ m}^2/\text{g}$ and an average particle diameter of 200 Å (produced by Daiichi Kigenso Kagaku K.K.), drying the resultant mixture overnight at 120°C, and then calcining the dried mixture in the air at 400°C for 2 hours.

A zirconia powder containing 9% by weight of rhodium was prepared by mixing an aqueous rhodium nitrate solution containing 0.3 g of rhodium and 3 g of the same zirconia as mentioned above, drying the resultant mixture overnight at 120°C, and then calcining the dried mixture in the air at 400°C for 2 hours.

An aqueous slurry for coating was prepared by severally pulverizing the platinum-containing zirconia powder and rhodium-containing zirconia powder in a mortar until an average particle diameter of about 20 microns, mixing the pulverized powders with 130 g of an activated alumina possessing a specific surface area of $100 \text{ m}^2/\text{g}$, and wet pulverizing the resultant mixture in a ball mill for 20 hours.

A finished catalyst was obtained by immersing the same monolithic carrier as used in Example 8 in the coating aqueous slurry, removing the carrier from the slurry, blowing the wet carrier with compressed air so as to relieve all the cells in the carrier of clogging slurry, and then drying the carrier at 130°C for 3 hours.

When the coating layer of this catalyst was examined by the same method as in Example 8, the 10 platinum-containing zirconia and the rhodium-containing zirconia were found to be dispersed both in the form of particles possessing an equal average particle diameter of 7 microns. This catalyst was found to contain 0.065 g of platinum and 0.013 g of rhodium per carrier piece.

15 Example 45

A zirconia powder containing 16.7% by weight of palladium was prepared by mixing an aqueous palladium nitrate solution containing 1.5g of palladium with 7.5 g of the same zirconia as used in Example 44, drying the 20 resultant mixture overnight at 120°C, and then calcining the dried mixture in the air at 400°C for 2 hours.

A finished catalyst was obtained by following the procedure of Example 44, excepting the palladium-containing zirconia powder was used in the 25 place of the platinum-containing zirconia powder.

When the coating layer of this catalyst was examined by the same method as in Example 8, the palladium-containing zirconia was found to be dispersed in the form of particles possessing an average particle 30 diameter of 5 microns and the rhodium-containing zirconia in the form of particles possessing an average particle diameter of 6 microns. This catalyst was found to contain 0.065 g of palladium and 0.013 g of rhodium per carrier piece.

35 Example 46

A zirconia powder containing 5% by weight of palladium was prepared by mixing 7.5 g of the same zirconia as used in Example 44 with a mixture of an aqueous platinic chloride solution containing 0.9 g of 5 platinum and an aqueous palladium chloride solution containing 0.6 g of palladium, drying the resultant mixture overnight at 120°C, and then calcining the dried mixture in the air at 400°C for 2 hours.

A finished catalyst was obtained by following 10 the procedure of Example 44, excepting the platinum- and palladium-containing zirconia powder was used in the place of the platinum-containing zirconia powder.

When the coating layer of the catalyst was examined by the same method as in Example 8, the 15 platinum- and palladium-containing zirconia was found to be dispersed in the form of particles possessing an average particle diameter of 13 microns and the rhodium-containing zirconia in the form of particles possessing an average particle diameter of 5 microns. 20 This catalyst was found to contain 0.039g of platinum, 0.026 g of palladium, and 0.013 g of rhodium per carrier piece.

Example 47

A finished catalyst was obtained by following 25 the procedure of Example 44, excepting a zirconia possessing a specific surface area of 90 m²/g and an average particle diameter of 150 Å (produced by Daiichi Kigenso Kagaku K.K.) was used in the place of the zirconia of Example 44

30 When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum-containing zirconia was found to be dispersed in the form of particles possessing an average particle diameter of 2 microns and the rhodium-containing 35 zirconia in the form of particles possessing an average

particle diameter of 6 microns. This catalyst was found to contain 0.065 g platinum and 0.013 g of rhodium per carrier piece.

Example 48

5 A finished catalyst was obtained by following the procedure of Example 44, excepting the same metallic monolithic carrier as used in Example 13 was used in the place of the monolithic carrier of cordierite of Example 44.

10 When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum-containing zirconia was found to be dispersed in the form of particles possessing an average particle diameter of 6 microns and the rhodium-containing 15 zirconia in the form of particles possessing an average particle diameter of 7 microns. This catalyst was found to contain 0.065 g of platinum and 0.013 g of rhodium per carrier piece.

Example 49

20 An alumina powder containing CeO_2 and Fe_2O_3 was obtained by dissolving 25.2 g of cerium nitrate $[\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$ and 10.1 g of ferric nitrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ in 100 g of purified water, mixing the resultant aqueous solution with 127 g of an activated alumina 25 possessing a specific surface area of $100 \text{ m}^2/\text{g}$, drying the resultant mixture overnight at 120°C , and then calcining the dried mixture in the air at 700°C for 1 hour.

30 A finished catalyst was obtained by following the procedure of Example 44, excepting the CeO_2 - and Fe_2O_3 -containing alumina was used in the place of 139 g of the activated alumina of Example 44.

35 When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum-containing zirconia and the rhodium-containing zirconia were found to be dispersed in the form of

particles possessing an equal average particle diameter of 5 microns. This catalyst was found to contain 0.065 g of platinum and 0.013 of rhodium per carrier piece.

Control 15

5 An aqueous slurry for coating was prepared by wet pulverizing 150 g of the same activated alumina possessing a specific surface area of 100 m^2/g as in Example 44.

10 A finished catalyst was obtained by coating the same monolithic carrier of cordierite as in Example 44 with 6.5 g as alumina of the aqueous slurry for coating, immersing the carrier coated with the activated alumina in a mixture of an aqueous solution of the nitrate of dinitro-diammine platinum, and an aqueous 15 solution of rhodium nitrate, removing the carrier from the solution, blowing the wet carrier with compressed air to remove excess aqueous solution, drying the wet carrier at 130°C for 3 hours, and calcining the dried carrier in the air at 400°C for 2 hours.

20 When the coating layer of this catalyst was examined by the same method as in Example 8, neither platinum nor rhodium was found to be dispersed in the form of particles exceeding 0.5 micron in diameter. This catalyst was found to contain 0.065 g of platinum 25 and 0.013 g of rhodium per carrier piece.

Control 16

30 An aqueous slurry for coating was prepared by wet pulverizing 150 g of the same zirconia possessing a specific surface area of 60 m^2/g and an average particle diameter of 200 Å as in Example 44.

A finished catalyst was obtained by coating the same monolithic carrier of cordierite as in Example 44 with 6.5 g as zirconia of the aqueous slurry for coating and depositing platinum and rhodium on the 35 carrier coated with zirconia by following the procedure of Control 15.

When the coating layer of this catalyst was examined by the same method as in Example 8, neither platinum nor rhodium was found to be dispersed in the form of particles exceeding 0.5 micron in diameter. This catalyst was found to contain 0.065 g of platinum and 0.013 g of rhodium per carrier piece.

Example 50

When the coating layer of this catalyst was examined by the same method as in Example 8, neither platinum nor rhodium was found to be dispersed in the form of particles exceeding 0.5 micron in diameter. This catalyst was found to contain 0.065 g of platinum and 0.013 g of rhodium per carrier piece.

The catalysts of Examples 44 through 49 and 15 the catalysts of Controls 15 and 16 were tested for catalytic property after aging in an electric furnace and for catalytic activity after endurance test in an engine in the same manner as in Example 15. The results are shown in Table 13 and Table 14.

Table 13 Evaluation of catalytic property
after aging in electric furnace

5	Catalyst	Purifying property at low temperatures		
		CO purifying temperature, T_{50} (°C)	HC purifying temperature, T_{50} (°C)	NO purifying temperature, T_{50} (°C)
10	Example 44	383	388	381
	45	375	381	374
	46	377	384	375
	47	381	386	379
	48	380	386	378
	49	378	385	375
	Control 15	456	460	455
	16	463	468	462

15 Table 14 Evaluation of catalytic property
after test run of engine

20	Catalyst	Purifying property at low temperatures		
		CO purifying temperature, T_{50} (°C)	HC purifying temperature, T_{50} (°C)	NO purifying temperature, T_{50} (°C)
25	Example 44	360	366	352
	45	375	382	369
	46	370	376	365
	47	361	365	353
	48	358	363	350
	49	362	368	354
	Control 15	438	455	453
	16	442	450	440

Example 51

A finished catalyst was obtained by following the procedure of Example 44, excepting 75 g of a commercially available cerium oxide powder (produced by 5 Nissan Kidogenso K.K.) was used in addition to the platinum-containing zirconia powder, rhodium-containing zirconia powder, and 139 g of the activated alumina of Example 44. When the coating layer of this catalyst was examined by the same method as in Example 8, the 10 platinum-containing zirconia and the rhodium-containing zirconia were found to be dispersed both in the form of particles possessing an average particle diameter of 7 microns. This catalyst was found to contain 0.065 g of 15 platinum and 0.013 g of rhodium per carrier piece.

15 Example 52

A zirconia powder containing 16.7% by weight of palladium was prepared by mixing an aqueous palladium nitrate solution containing 1.5 g of palladium with 7.5 g of the same zirconia as used in Example 51, drying the 20 resultant mixture overnight at 120°C, and then calcining the dried mixture in the air at 400°C for 2 hours.

A finished catalyst was obtained by following the procedure of Example 51, excepting the 25 palladium-containing zirconia powder was used in the place of the platinum-containing zirconia powder of Example 51. When the coating layer of this catalyst was examined by the same method as in Example 8, the palladium-containing zirconia was found to be dispersed in the form of particles possessing an average particle 30 diameter of 5 microns and the rhodium-containing zirconia in the form of particles possessing an average particle diameter of 6 microns. This catalyst was found to contain 0.065 g of palladium and 0.013 g of rhodium per carrier piece.

35 Example 53

A zirconia powder containing 10% by weight of platinum and 6.7% by weight of palladium was prepared by mixing 7.5 g of the same zirconia as used in Example 51 with a mixture of an aqueous platinic chloride solution 5 containing 0.9 g of platinum and an aqueous palladium chloride solution containing 0.6 g of palladium, drying the resultant mixture overnight at 120°C, and then calcining the dried mixture in the air at 400°C for 2 hours.

10 A finished catalyst was obtained by following the procedure of Example 51, excepting the platinum- and palladium-containing zirconia powder was used in the place of platinum-containing zirconia powder of Example 51.

15 When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum- and palladium-containing zirconia was found to be dispersed in the form of particles possessing an average particle diameter of 13 microns and the 20 rhodium-containing zirconia in the form of particles possessing an average particle diameter of 5 microns. This catalyst was found to contain 0.039 g of platinum, 0.026 g of palladium, and 0.013 g of rhodium per catalyst piece.

25 Example 54

A finished catalyst was obtained by following the procedure of Example 51, excepting a zirconia possessing a specific surface area of 90m²/g and an average particle diameter of 150 Å (produced by Daiichi 30 Kigenso Kagaku K.K.) was used in the place of zirconia of Example 51.

When the coating layer of this catalyst was examined by the same method as in Example 8. The platinum-containing zirconia was found to be dispersed 35 in the form of particles possessing an average particle

diameter of 0.5 micron and the rhodium-containing zirconia in the form of particles possessing an average particle diameter of 1 micron.

Example 55

5 A finished catalyst was obtained by following the procedure of Example 51, excepting the same metallic monolithic carrier as used in Example 13 was used in the place of the monolithic carrier of cordierite of Example 51.

10 When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum-containing zirconia was found to be dispersed in the form of particles possessing an average particle diameter of 6 microns and the rhodium-containing zirconia in the form of particles possessing an average particle diameter of 7 microns. This catalyst was found to contain 0.065 g of platinum and 0.013 g of rhodium per carrier piece.

Example 56

20 An alumina powder containing CeO_2 and Fe_2O_3 was obtained by dissolving 25.2 g of cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and 10.1 g of ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) in 100 g of purified water, mixing the resultant solution with 127 g of an activated alumina possessing a 25 specific surface area of $100 \text{ m}^2/\text{g}$, drying the resultant mixture overnight at 120°C , and then calcining the dried mixture in the air at 700°C for 1 hour.

A finished catalyst was obtained by following the procedure of Example 51, excepting the alumina 30 containing CeO_2 and Fe_2O_3 was used in the place of 139 g of the activated alumina of Example 51.

When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum-containing zirconia and the rhodium-containing 35 zirconia were found to be dispersed both in the form of

particles possessing an average particle diameter of 5 microns. This catalyst was found to contain 0.065 g of platinum and 0.013 g of rhodium per carrier piece.

Example 57

5 A finished catalyst was obtained by following the procedure of Example 51, excepting 75 g of the same alumina-modified cerium oxide as in Example 21 was used in the place of the commercially available cerium oxide powder of Example 51.

10 When the coating layer of this catalyst was examined by the same method as in Example 8, the same platinum-containing zirconia and the rhodium-containing zirconia were found to be dispersed both in the form of particles possessing an equal average particle diameter 15 of 3 microns. This catalyst was found to contain 0.065 g of platinum and 0.013 g of rhodium per carrier piece.

Example 58

20 A finished catalyst was obtained by following the procedure of Example 51, excepting 75 g of the same alumina-modified cerium oxide as in Example 22 was used in the place of the commercially available cerium oxide powder of Example 51.

25 When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum-containing zirconia and the rhodium-containing zirconia were found to be dispersed both in the form of particles possessing an equal average particle diameter 30 of 6 microns. This catalyst was found to contain 0.065 g of platinum and 0.013 g of rhodium per carrier piece.

30 Example 59

35 A finished catalyst was obtained by following the procedure of Example 51, excepting 75 g of the same alumina-modified cerium oxide as in Example 23 was used in the place of the commercially available cerium oxide powder of Example 51.

When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum-containing zirconia and the rhodium-containing zirconia were found to be dispersed both in the form of 5 particles possessing an equal average particle diameter of 1 micron. This catalyst was found to contain 0.065 g of platinum and 0.013 g of rhodium per carrier piece.

Control 17

An aqueous slurry for coating was prepared by 10 wet pulverizing 150 g of the same activated alumina possessing a specific surface area of 100 m^2/g as used in Example 51 and 75 g of a commercially available cerium oxide powder in a ball mill for 20 hours.

A finished catalyst was obtained by coating 15 the same monolithic carrier of cordierite as obtained in Example 51 with the aqueous slurry for coating, immersing the carrier coated with the activated alumina and the cerium oxide in a mixture of an aqueous solution of the nitrate of dinitro-diammine platinum and an 20 aqueous rhodium nitrate solution, removing the carrier from the mixture, blown with compressed air to remove excess solution, drying the wet carrier at 130°C for 3 hours, and then calcining the dried carrier in the air at 400°C for 2 hours.

25 When the coating layer of this catalyst was examined by the same method as in Example 8, neither platinum nor rhodium was found to be dispersed in the form of particles exceeding 0.5 micron. This catalyst was found to contain 0.065 g of platinum and 0.013 g of 30 rhodium per carrier piece.

Control 18

An aqueous slurry for coating was prepared by wet pulverizing 150 g of the same zirconia possessing a specific surface area of 60 m^2/g and an average particle 35 diameter of 200 Å and 75 g of a commercially available cerium oxide powder in a ball mill for 20 hours.

A finished catalyst was obtained by coating the same monolithic carrier of cordierite as used in Example 51 with the aqueous slurry for coating and depositing platinum and rhodium on the carrier coated 5 with zirconia and cerium oxide by following the procedure of Control 17.

When the coating layer of this catalyst was examined by the same method as in Example 8, neither platinum nor rhodium was found to be dispersed in the 10 form of particles exceeding 0.5 micron in diameter. This catalyst was found to contain 0.065 g of platinum and 0.013 g of rhodium.

Example 60

The catalysts of Examples 51 through 59 and 15 the catalysts of Controls 17 and 18 were tested for catalytic property after aging in an electric furnace and for catalytic activity after endurance test in an engine in the same manner as in Example 15. The results are shown in Tables 15 and 16.

Table 1.5 Evaluation of catalytic property
after aging in electric furnace

Catalyst	Three way performance		Purifying property at low temperatures		
	Crossover point		CO purifying temperature	HC purifying temperature	NO purifying temperature
	CO, NO purify-ing ratio(%)	HC purify-ing ratio(%)	T_{50} (°C)	T_{50} (°C)	T_{50} (°C)
Example 51	88	89	380	385	377
	52	90	374	380	370
	53	88	378	384	375
	54	87	381	385	376
	55	88	377	381	374
	56	86	385	390	382
	57	93	367	372	365
	58	92	369	373	365
	59	91	370	375	367
Control 17	61	66	445	449	443
	18	58	450	455	448

Table 16 Evaluation of catalytic property
after test run of engine

Catalyst	Three way performance		Purifying property at low temperatures		
	Crossover point	CO purifying temperature	HC purifying temperature	NO purifying temperature	
	CO, NO purifying ratio(%)	HC purifying ratio(%)	T_{50} (°C)	T_{50} (°C)	T_{50} (°C)
Example 51	86	92	355	360	349
52	83	90	365	372	360
53	85	92	362	370	355
54	86	93	352	358	345
55	87	93	356	362	349
56	88	94	353	359	345
57	94	98	340	345	333
58	92	97	344	350	336
59	92	96	343	348	335
Control 17	70	81	395	402	390
18	65	76	401	410	395

It is clearly noted from Tables 15 and 16 that the catalysts of Examples 51 through 59 in which zirconia powders having platinum, palladium, and rhodium deposited in high ratios contemplated by the present invention were dispersed in coating layers in the form of coherent particles possessing an average particle diameter in the range of 0.5 to 20 microns invariably exhibited better catalytic properties than the catalysts of Controls 17 and 18. The catalysts of Examples 57 through 59 which used alumina-modified cerium oxides exhibited still better properties.

Example 61

A zirconia powder containing 16.1% by weight of platinum and 3.2% by weight of rhodium was prepared by mixing 7.5 g of a zirconia possessing a specific surface area of $60 \text{ m}^2/\text{g}$ and an average particle diameter

of 200 Å (produced by Daiichi Kigenso Kagaku K.K.) with a mixture of an aqueous solution of the nitrate of dinitro-diammine platinum containing 1.5 g of platinum and an aqueous rhodium nitrate solution containing 0.3 g of rhodium, drying the resultant mixture overnight at 120°C, and then calcining the dried mixture in the air at 400°C for 2 hours.

An aqueous slurry for coating was prepared by pulverizing the platinum- and rhodium-containing zirconia powder in a mortar until coherent particles possessing an average particle diameter of about 20 microns were formed, mixing the pulverized powder with 139 g of an activated alumina possessing a specific surface area of 100 m²/g, and wet pulverizing the resultant mixture in a ball mill for 20 hours.

A finished catalyst was obtained by immersing the same monolithic carrier as used in Example 8 in the aqueous slurry for coating, removing the carrier from the slurry, blowing the wet carrier with compressed air to relieve all the cells of the carrier of clogging slurry, and drying the coated carrier at 130°C for 3 hours.

When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum- and rhodium-containing zirconia was found to be dispersed in the form of particles possessing an average particle diameter 7 microns. This catalyst was found to contain 0.065 g of platinum and 0.013 g of rhodium per carrier piece.

30 Example 62

A zirconia powder containing 16.1% by weight of palladium and 3.2% by weight of rhodium was prepared by mixing 7.5 g of the same zirconia as used in Example 1 with a mixture of an aqueous palladium nitrate solution containing 1.5 g of palladium and an aqueous rhodium nitrate solution containing 0.3 g of rhodium,

dryng the resultant mixture overnight at 120°C, and then calcining the dried mixture in the air at 400°C for 2 hours.

A finished catalyst was obtained by following 5 the procedure of Example 61, excepting the palladium- and rhodium-containing zirconia powder was used in the place of the platinum- and rhodium-containing zirconia powder of Example 61.

When the coating layer of this catalyst was 10 examined by the same method as in Example 8, the platinum- and rhodium-containing zirconia was found to be dispersed in the form of particles possessing an average particle diameter of 3 microns. This catalyst was found to contain 0.065 g of palladium and 0.013 g of 15 rhodium.

Example 63

A zirconia powder containing 9.7% by weight of platinum, 6.5% by weight of palladium, and 3.2% by weight of rhodium was prepared by mixing 7.5 g of the same 20 zirconia as used in Example 61 with a mixture of an aqueous platinic chloride solution containing 0.9 g of platinum, and aqueous palladium chloride solution containing 0.6 g of palladium, and an aqueous rhodium nitrate solution containing 0.3 g of rhodium, drying the 25 resultant mixture overnight at 120°C, and then calcining the dried mixture in the air at 400°C for 2 hours.

A finished catalyst was obtained by following the procedure of Example 61, excepting the platinum-, palladium-, and rhodium-containing zirconia powder were 30 used in the place of platinum- and rhodium-containing zirconia of Example 61.

When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum-, palladium-, and rhodium-containing zirconia 35 was found to be dispersed in the form of particles possessing an average particle diameter of 13 microns.

This catalyst was found to contain 0.093 g of platinum, 0.026 g of palladium, and 0.013 g of rhodium per carrier piece.

Example 64

5 A finished catalyst was obtained by following the procedure of Example 61, excepting a zirconia possessing a specific surface area of 90 m²/g and an average particle diameter of 150 Å (produced by Daiichi Kigenso Kagaku K.K.) was used in the place of the 10 zirconia of Example 61.

When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum- and rhodium-containing zirconia was found to be dispersed in the form of particles possessing an 15 average particle diameter of 2 microns. This catalyst was found to contain 0.065 g of platinum and 0.013 g of rhodium per carrier piece.

Exmaple 65

20 A finished catalyst was obtained by following the procedure of Example 61, excepting the same metallic carrier as used in Example 13 was used in the place of the monolithic carrier of cordierite of Example 61.

When the coating layer of this catalyst was examined by the same method as in Exámplo 8, the 25 platinum- and rhodium-containing zirconia was found to be dispersed in the form of particles possessing an average particle diameter of 6 microns. This catalyst was found to contain 0.065 g of platinum and 0.013 g of rhodium per carrier piece.

30 Example 66

An alumina powder containing CeO₂ and Fe₂O₃ was obtained by dissolving 25.2 g of cerium nitrate (Ce(NO₃)₃ · 6H₂O) and 10.1 g of ferric nitrate (Fe(NO₃)₃ · 9H₂O) in 100 g of purified water, mixing the resultant 35 solution with 127 g of an activated alumina possessing

a specific surface area of 100 m^2/g , drying the resultant mixture overnight at 120°C, and then calcining the dried mixture in the air at 700°C for 1 hour.

A finished catalyst was obtained by following 5 the procedure of Example 61, excepting the CeO_2 - and Fe_2O_3 - containing alumina was used in the place of 139 g of the activated alumina of Example 61.

When the coating layer of this catalyst was examined by the same method as in Example 8, the 10 platinum- and rhodium-containing zirconia was found to be dispersed in the form of particles possessing an average particle diameter of 5 microns. This catalyst was found to contain 0.065 g of platinum and 0.013 g of rhodium per carrier piece.

15 Control 19

An aqueous slurry for coating was prepared by wet pulverizing 150 g of the same activated alumina possessing a specific surface area of 100 m^2/g as used in Example 61 in a ball mill for 20 hours.

20 A finished catalyst was obtained by coating the same monolithic carrier of cordierite with 6.5 g of alumina of the aqueous slurry for plating in the same manner as in Example 61, immersing the carrier coated with the activated alumina in a mixture of an aqueous 25 solution of the nitrate of dinitro-diammine platinum and an aqueous rhodium nitrate solution, removing the carrier from the mixture, blowing the wet carrier with compressed air to remove excess aqueous solution, drying the wet carrier at 130°C for 3 hours, and calcining the 30 dried carrier in the air at 400°C for 2 hours.

When the coating layer of this catalyst was examined by the same method as in Example 8, neither platinum nor rhodium was found to be dispersed in the form of particles exceeding 0.5 micron in diameter. 35 This catalyst was found to contain 0.065 g of platinum and 0.013 g of rhodium per carrier piece.

Control 20

An aqueous slurry for coating was prepared by wet pulverizing 150 g of the same zirconia possessing a specific surface area of $60 \text{ m}^2/\text{g}$ and an average particle diameter of 200 Å as used in Example 61 in a ball mill 5 for 2 hours.

A finished catalyst was obtained by coating a monolithic carrier of cordierite with 6.5 g of zirconia of the aqueous slurry for coating in the same manner as in Example 61 and depositing platinum and rhodium on the 10 carrier coated with the zirconia in the same manner as in Control 19.

When the coating layer of this catalyst was examined by the same method as in Example 8, neither platinum nor rhodium was found to be dispersed in the 15 form of particles exceeding 0.5 micron in diameter. This catalyst was found to contain 0.065 g of platinum and 0.013 g of rhodium per carrier piece.

Example 67

The catalysts of Examples 61 through 66 and 20 the catalysts of Controls 19 and 20 were tested for catalytic property after aging in an electric furnace and for catalytic activity after endurance test in an engine in the same manner as in Example 15. The results are shown in Table 17 and Table 18.

Table 17 Evaluation of catalytic property after aging in electric furnace

Catalyst	Purifying property at low temperatures		
	CO purifying temperature, T ₅₀ (°C)	HC purifying temperature, T ₅₀ (°C)	NO purifying temperature, T ₅₀ (°C)
Example 61	375	381	372
	370	376	368
	372	378	370
	374	380	372
	373	379	372
	376	382	372
	456	460	455
Control 19			
20	463	468	462

Table 18 Evaluation of catalytic property after test run of engine

Catalyst	Purifying property at low temperatures		
	CO purifying temperature, T ₅₀ (°C)	HC purifying temperature, T ₅₀ (°C)	NO purifying temperature, T ₅₀ (°C)
Example 61	354	360	347
	365	372	359
	363	370	356
	355	360	347
	352	358	344
	355	361	347
	438	445	435
Control 19			
20	442	450	440

It is clearly noted from Table 17 and Table 18 that the catalyst of Examples 61 through 66 in which zirconia powders having platinum, palladium, and rhodium deposited in high ratios contemplated by this invention disposed in the coating layers in the form of particles possessing an average particle diameter in the range of 0.1 to 20 microns invariably exhibited better catalytic properties than the catalysts of Controls 19 and 20 which had noble metals deposited in the conventional state.

Example 68

A finished catalyst was obtained by following the procedure of Example 61 excepting 75 g of a commercially available cerium oxide (produced by Nissa 15 Kidogenso K.K.) was used in addition to the platinum- and rhodium-containing zirconia powder and 139 g of the activated alumina of Example 61. When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum- and rhodium-containing zirconia 20 was found to be dispersed in the form of particles possessing an average particle diameter of 7 microns. This catalyst was found to contain 0.065 g of platinum and 0.013 g of rhodium per carrier piece.

Example 69

25 A zirconia powder containing 16.1% by weight of palladium and 3.2% by weight of rhodium was prepared by mixing 7.5 g of the same zirconia as used in Example 68 with a mixture of an aqueous palladium nitrate solution containing 1.5 g of palladium and an aqueous 30 rhodium nitrate solution containing 0.3 g of rhodium, drying the resultant mixture overnight at 120°C, then calcining the dried mixture in the air at 400°C for 2 hours.

A finished catalyst was obtained by following the procedure of Example 68, excepting the palladium- and rhodium-containing zirconia powder was used in the place of platinum- and rhodium-containing zirconia 5 powder of Example 68.

When the coating layer of this catalyst was examined by the same method as in Example 8, the palladium- and rhodium-containing zirconia was found to be dispersed in the form of particles possessing an 10 average particle diameter of 3 microns. This catalyst was found to contain 0.065 g of palladium and 0.013g of rhodium per carrier piece.

Example 70

A zirconia powder containing 9.7% by weight of 15 platinum, 6.5% by weight of palladium, and 3.2% by weight of rhodium was prepared by mixing 7.5 g of the same zirconia as used in Example 68 with a mixture of an aqueous platinic chloride solution containing 0.9 g of platinum, an aqueous palladium chloride solution 20 containing 0.6 g of palladium, and an aqueous rhodium nitrate solution containing 0.3 g of rhodium, drying the resultant mixture overnight at 120°C, and then calcining the dried mixture in the air at 400°C for 2 hours.

A finished catalyst was obtained by following 25 the procedure of Example 68, excepting the platinum-, palladium-, and rhodium-containing zirconia powder was used in the place of the platinum- and rhodium-containing zirconia powder of Example 68.

When the coating layer of this catalyst was 30 examined by the same method as in Example 8, the platinum-, palladium-, and rhodium-containing zirconia was found to be dispersed in the form of particles possessing an average particle diameter of 13 microns. This catalyst was found to contain 0.039 g of platinum, 35 0.026 g of palladium, and 0.013 g of rhodium per carrier piece.

Example 71

A finished catalyst was obtained by following the procedure of Example 68, excepting a zirconia possessing a specific surface area of $90\text{ m}^2/\text{g}$ and an average particle diameter of 150 \AA (produced by Daiichi 5 Kigenso Kagaku K.K.) was used in the place of the zirconia of Example 68.

When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum- and rhodium-containing zirconia was found to 10 be dispersed in the form of particles possessing an average particle diameter of 2 microns. This catalyst was found to contain 0.065 g of platinum and 0.013 g rhodium per carrier piece.

Example 72

15 A finished catalyst was obtained by following the procedure of Example 68, excepting the same metallic monolithic carrier as used in Example 18 was used in the place of the monolithic carrier of cordierite of Example 68.

20 When the coating layer of this catalyst was examined by the same method as in Example 8, the platinum- and rhodium-containing zirconia was found to be dispersed in the form of particles possessing an average particle diameter of 6 microns. This catalyst 25 was found to contain 0.065 g of platinum and 0.013 g of rhodium per carrier piece.

Example 73

An alumina powder containing CeO_2 and Fe_2O_3 was obtained by dissolving 25.2 g of cerium nitrate 30 ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and 10.1 g of ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) in 100 g of purified water, mixing the resultant solution with 127 g of an activated alumina possessing a specific surface area of $100\text{ m}^2/\text{g}$, drying the resultant mixture overnight at 120°C , and then calcining the dried 35 mixture in the air at 700°C for 1 hour.

A finished catalyst was obtained by following the procedure of Example 65, excepting the CeO_2 - and Fe_2O_3 -containing alumina was used in the place of 139 g of the activated alumina of Example 68.

5 When the coating layer of this catalyst was examined by the same method as in Example 8, the same platinum- and rhodium-containing zirconia was found to be dispersed in the form of particles possessing an average particle diameter of 5 microns. This catalyst 10 was found to contain 0.065 g of platinum and 0.013 g of rhodium.

Example 74

A finished catalyst was obtained by following the procedure of Example 68, excepting 75 g of the same 15 alumina-modified cerium oxide as in Example 21 was used in the place of the commercially available cerium oxide used in Example 68.

When the coating layer of this catalyst was examined by the same method as in Example 8, the same 20 platinum-containing zirconia and the rhodium-containing zirconia were found to be dispersed both in the form of particles possessing an equal average particle diameter of 3 microns. This catalyst was found to contain 0.065 g of platinum and 0.013 g of rhodium per carrier piece.

25 Example 75

A finished catalyst was obtained by following the procedure of Example 68, excepting 75 g of the same 30 alumina-modified cerium oxide as in Example 22 was used in the place of the commercially available cerium oxide powder used in Example 68.

When the coating layer of the catalyst was examined by the same method as in Example 8, the platinum-containing zirconia and the rhodium-containing zirconia were found to be dispersed both in the form of 35 particles possessing an equal average particle diameter of 1 microns. This catalyst was found to contain 0.065 g of platinum and 0.013 g of rhodium per carrier piece.

Example 76

A finished catalyst was obtained by following the procedure of Example 68, excepting 75 g of the same alumina-modified cerium oxide as in Example 23 was used 5 in the place of the commercially available cerium oxide powder used in Example 68.

When the coating layer of the catalyst was examined by the same method as in Example 8, the platinum-containing zirconia and the rhodium-containing 10 zirconia were found to be dispersed both in the form of particle possessing an equal average particle diameter of 1 microns. This catalyst was found to contain 0.065 g of platinum and 0.013 g of rhodium per carrier piece.

Control 21

15 An aqueous slurry for coating was prepared by wet pulverizing 150 g of the same activated alumina possessing a specific surface area of $100 \text{ m}^2/\text{g}$ as used in Example 68 and 75 g of a commercially available cerium oxide powder in a ball mill for 20 hours.

20 A finished catalyst was obtained by coating a monolithic carrier of cordierite with the aqueous slurry for coating in the same manner as in Example 68, immersing the carrier coated with the activated alumina and the cerium oxide in a mixture of an aqueous solution 25 of the nitrate of dinitro-diammine platinum and an aqueous rhodium nitrate solution, removing the carrier from the mixture, blowing the carrier with compressed air to remove excess solution, drying the wet carrier at 130°C for 3 hours, and then calcining the dried carrier 30 in the air at 400°C for 2 hours.

When the coating layer of this catalyst was examined by the same method as in Example 8, neither platinum nor rhodium was found to be dispersed in the form of particles exceeding 0.5 micron in diameter. 35 This catalyst was found to contain 0.065 g of platinum and 0.013 g of rhodium per carrier piece.

Control 22

An aqueous slurry for coating was prepared by wet pulverizing 150 g of the same zirconia possessing specific surface area of 60 m^2/g and an average particle diameter of 200 Å as used in Example 68 and 75 g a 5 commercially available cerium oxide powder in a ball mill for 20 hours.

A finished catalyst was obtained by coating a monolithic carrier of cordierite with the aqueous slurry for coating in the same manner as in Example 68 and 10 depositing platinum and rhodium on the carrier coated with the zirconia and the cerium oxide in the same manner as in Control 21.

When the coating layer of this catalyst was examined by the same method as in Example 8, neither 15 platinum nor rhodium was found to be dispersed in the form of particles exceeding 0.5 micron in diameter. This catalyst was found to contain 0.065 g of platinum and 0.013 g of rhodium per carrier piece.

Example 77

20 The catalysts of Examples 68 through 76 and the catalysts of Controls 21 and 22 were tested for catalytic property after aging in an electric furnace and for catalytic activity after endurance test in an engine in the same manner as in Example 15. The 25 results are shown in Table 19 and 20.

Table 19 Evaluation of catalytic property
after aging in electric furnace

Catalyst	Three way performance		Purifying property at low temperatures		
	Crossover point		CO purifying temperature	HC purifying temperature	NO purifying temperature
	CO, NO purifying ratio(%)	HC purifying ratio(%)	T_{50} (°C)	T_{50} (°C)	T_{50} (°C)
Example 68	90	91	375	380	372
69	91	93	370	376	367
70	90	92	374	380	370
71	88	90	377	381	374
72	89	91	372	377	369
73	87	88	380	386	377
74	95	96	361	366	356
75	93	95	363	368	359
76	93	94	362	368	357
Control 21	61	66	445	449	443
22	58	63	450	455	448

Table 20 Evaluation of catalytic property
after test run of engine

Catalyst	Three way performance		Purifying property at low temperatures		
	Crossover point	CO purifying temperature	HC purifying	NO purifying temperature	
			temperature		
	CO, NO purify- ing ratio(%)	HC purify- ing ratio(%)	T ₅₀ (°C)	T ₅₀ (°C)	T ₅₀ (°C)
5	Example 68	88	94	347	352
		69	85	358	365
		70	87	353	360
		71	88	343	350
10	72	89	95	346	353
	73	89	94	343	349
	74	96	98	338	344
	75	94	97	342	348
	76	94	97	341	346
15	Control 21	70	81	395	402
	22	65	76	401	410
20					395

It is clearly noted from Table 19 and Table 20 that the catalysts of Examples 68 through 76 in which zirconia powders having platinum, palladium, and rhodium 25 deposited in high ratios as contemplated by the present invention were dispersed in the coating layers in the form of coherent particles having an average particle diameter in the range of 0.5 to 20 microns invariably exhibited very satisfactory catalytic properties as 30 compared with the catalyst of Controls 21 and 22 which had noble metals deposited in the conventional state.

The catalysts of Examples 74 through 76 which used alumina-modified cerium oxides exhibited still better catalytic properties.

From the results given above, it is clear that the catalysts of the present invention incur only slight deterioration and possess outstanding durability under ordinary operating conditions of engine and even under 5 harsh conditions as under a high-temperature oxidative atmosphere.

The claims form part of the disclosure of this specification.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A catalyst for purifying exhaust gas comprising a honeycomb carrier of monolithic structure and a coating layer applied on said honeycomb carrier and formed with a catalyst composition comprising a platinum group metal-supporting zirconia produced by depositing said platinum group metal on zirconia powder, a refractory inorganic oxide, and a rare earth metal oxide, said platinum group metal is at least one member selected from the group consisting of (a) rhodium, (b) combination of rhodium and platinum, (c) combination of rhodium and palladium, and (d) combination of rhodium, platinum, and palladium, and is deposited in proportion in the range of 0.5 to 30% by weight on said zirconia powder.
2. A catalyst according to claim 1, wherein said zirconia powder has a specific surface area of at least 10 m²/g and an average particle diameter of not more than 2,000 Å as primary particles.
3. A catalyst according to claim 1, wherein the content of said zirconia powder in said catalyst composition is in the range of 0.5 to 50% by weight.
4. A catalyst according to claim 1, wherein said refractory inorganic oxide is activated alumina.
5. A catalyst according to claim 1, wherein said refractory inorganic oxide contains at least one member selected from the group consisting of cerium, lanthanum, and neodymium in proportion in the range of 0.1 to 30% by weight to said refractory inorganic oxide.
6. A catalyst according to claim 5, wherein said refractory inorganic oxide is activated alumina.
7. A catalyst according to claim 1, wherein said rare earth metal oxide is cerium oxide.
8. A catalyst according to claim 7, wherein the content of cerium oxide in said catalyst composition is in the range of 5 to 80% by weight.
9. A method for the production of a catalyst for purifying exhaust gas, which comprises coating a honeycomb carrier of monolithic structure with an aqueous slurry containing a platinum group metal-carrying zirconia, refractory inorganic oxide, and a rare earth metal oxide and

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calcining the resultant coated carrier, said platinum group metal is at least one member selected from the group consisting of (a) rhodium, (b) combination of rhodium and platinum, (c) combination of rhodium and palladium, and (d) combination of rhodium, platinum, and palladium and is deposited in a proportion in the range of 0.5 to 30% by weight on said zirconia powder.

10. A catalyst for purifying exhaust gas, substantially as hereinbefore described with reference to any one of the specific Examples.

11. A method for the production of a catalyst substantially as hereinbefore described with reference to any one of the specific Examples.

DATED this 20 August 1990

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10/589,669	Metal Oxide Particle, Production Process Thereof and Exhaust Gas Purifying Catalyst	12-03-2010::11:17:24
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Bibliographic Data

Application Number:	10/589,669	Customer Number:	25944
Filing or 371 (c) Date:	08-16-2006	Status:	Docketed New Case - Ready for Examination
Application Type:	Utility	Status Date:	10-20-2010
Examiner Name:	ZIMMER, ANTHONY J	Location:	ELECTRONIC
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First Named Inventor:	Masahide Miura , Imasato-shi, (JP)	Issue Date of Patent:	-

Title of Invention: Metal Oxide Particle, Production Process Thereof and Exhaust Gas Purifying Catalyst

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10/589,669	Metal Oxide Particle, Production Process Thereof and Exhaust Gas Purifying Catalyst	12-03-2010:11:17:31
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Transaction History

Date	Transaction Description
10-20-2010	Date Forwarded to Examiner
10-19-2010	Request for Continued Examination (RCE)
10-20-2010	Disposal for a RCE / CPA / R129
10-19-2010	Request for Extension of Time - Granted
10-19-2010	Workflow - Request for RCE - Begin
10-06-2010	Case Docketed to Examiner in GAU
06-25-2010	Information Disclosure Statement (IDS) Filed
06-25-2010	Information Disclosure Statement (IDS) Filed
06-25-2010	Information Disclosure Statement (IDS) Filed
05-19-2010	Electronic Review
05-19-2010	Email Notification
05-19-2010	Mail Final Rejection (PTOL - 326)
05-17-2010	Final Rejection
12-01-2009	Information Disclosure Statement considered
03-11-2010	Date Forwarded to Examiner
02-11-2010	Response after Non-Final Action
12-01-2009	Reference capture on IDS
12-01-2009	Information Disclosure Statement (IDS) Filed
12-01-2009	Information Disclosure Statement (IDS) Filed
11-18-2009	Mail Non-Final Rejection
11-16-2009	Non-Final Rejection
09-28-2009	Information Disclosure Statement considered
09-28-2009	Reference capture on IDS
09-28-2009	Information Disclosure Statement (IDS) Filed
10-08-2009	Date Forwarded to Examiner
09-28-2009	Affidavit(s) (Rule 131 or 132) or Exhibit(s) Received
10-08-2009	Date Forwarded to Examiner
09-28-2009	Request for Continued Examination (RCE)
10-08-2009	Disposal for a RCE / CPA / R129
09-28-2009	Request for Extension of Time - Granted
09-28-2009	Information Disclosure Statement (IDS) Filed
09-28-2009	Workflow - Request for RCE - Begin
08-27-2009	Mail Examiner Interview Summary (PTOL - 413)
08-26-2009	Examiner Interview Summary Record (PTOL - 413)
04-28-2009	Mail Final Rejection (PTOL - 326)
04-27-2009	Final Rejection
02-26-2009	Date Forwarded to Examiner
02-04-2009	Response after Non-Final Action
11-05-2008	Mail Non-Final Rejection
11-04-2008	Non-Final Rejection
08-16-2006	Information Disclosure Statement considered
05-27-2008	Information Disclosure Statement considered

10-14-2008 Date Forwarded to Examiner
09-12-2008 Response to Election / Restriction Filed
08-12-2008 Mail Restriction Requirement
08-08-2008 Requirement for Restriction / Election
07-23-2008 Filing Receipt - Corrected
05-27-2008 Reference capture on IDS
05-27-2008 Information Disclosure Statement (IDS) Filed
05-27-2008 Information Disclosure Statement (IDS) Filed
02-28-2008 PG-Pub Issue Notification
02-07-2008 Case Docketed to Examiner in GAU
01-17-2008 Case Docketed to Examiner in GAU
12-30-2007 IFW TSS Processing by Tech Center Complete
05-16-2007 Miscellaneous Incoming Letter
11-16-2007 Miscellaneous Incoming Letter
11-19-2007 Request for Foreign Priority (Priority Papers May Be Included)
08-16-2006 Information Disclosure Statement (IDS) Filed
08-16-2006 Preliminary Amendment
08-16-2006 Information Disclosure Statement (IDS) Filed
12-07-2007 Filing Receipt - Corrected
11-29-2007 Application Dispatched from OIPE
11-20-2007 Sent to Classification Contractor
11-20-2007 Filing Receipt
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09-08-2006 Cleared by OIPE CSR
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